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Sulfur Dioxide Emission Control Technology Assessment

Part I — Magnesium Based Wet Scrubbing: Bench-Scale Study at a Sour Gas Plant

Alberta
ENVIRONMENTAL CENTRE

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SULFUR DIOXIDE EMISSION CONTROL TECHNOLOGY ASSESSMENT

PART I - MAGNESIUM BASED WET SCRUBBING: BENCH-SCALE STUDY AT A SOUR GAS PLANT

ALBERTA ENVIRONMENTAL CENTRE
Vegreville, Alberta

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SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Wet scrubbing processes for sulfur dioxide (SO_2) emission control that are currently in commercial operation could be broadly classified into two groups. In the "throw-away" group, the scrubber products are simply disposed of, whereas in the "regenerative" group, these are processed to regenerate the scrubbing media and to produce saleable by-products.

This report describes an assessment of a concept which combines the advantages of these two groups of processes, namely the production of directly saleable scrubber products. Thus, the resulting process would have the benefits of the lower capital cost and energy consumption of a "throw-away" process and the product sale revenue of a "regenerative" process, but without the associated disadvantages of disposal problems and high regeneration cost, respectively.

The two main areas of uncertainty were SO_2 removal efficiency and product quality. The latter was of particular concern due to the unknown effect of flue gas impurities, which could adversely affect the sale value of the products. Hence, it was imperative that this assessment include on-site tests at an industrial emission source.

The scope of this assessment was limited to:

(1) Laboratory and bench-scale tests These were carried out to assess process feasibility and to determine whether further development to pilot- or demonstration-scale operation would be warranted.

(2) The use of magnesium oxide (MgO) as the scrubbing medium This was selected on the basis of local availability and potential applications of the products in the agriculture, construction materials and wood pulping industries.

(3) The emission from the incinerator for Claus tail gas at a sour gas plant This was selected partly on the basis of the importance of the industry and the likelihood of low impurity contents in the flue gas.

Wet scrubbing of SO_2 gas with MgO is based on the use of magnesium sulphite as the active scrubbing agent. This reacts with dissolved SO_2 to form magnesium

bisulphite, into which MgO is added to form the active scrubbing agent. Depending on the mode of the operation either magnesium bisulphite or magnesium sulphite could be produced. The latter could be oxidized to form magnesium sulphate.

The bench-scale scrubber system consisted of 51 mm diameter turbulent contactor columns (instead of the conventional static packed bed), where the gas and the scrubbing slurry came into contact counter-currently; a gas quencher to cool the flue gas prior to entry into the columns; a recirculation system for the scrubbing slurry; a make-up slurry system for feeding slaked magnesium oxide; and an induced draft fan for withdrawing a slip stream of the incinerator flue gas. The nominal gas throughput was about 0.007 Nm^3/s.

Monitoring of the scrubber operation included measurements of SO_2, CO_2 (carbon dioxide) and O_2 (oxygen) concentrations, gas and slurry flow rates, column pressure drop, temperatures and pressures at various locations in the system, and chemical analyses of the scrubbing slurry. The precipitate formed in the scrubbing slurry was used to characterize the scrubber product quality.

A total of about 130 hours of on-site tests were carried out, producing the following results:

(1) <u>SO_2 removal efficiency</u> Values of 95 - 99% were obtained under the following conditions: total column pressure drop 1.5 - 2.5 kPa; liquid to gas flow ratio 2.5 to 5.5 L/m^3; scrubbing slurry pH 5.5 - 8.5 and total solids concentration 2-3 wt.%; and inlet SO_2 concentrations up to 15,000 ppm.

(2) <u>Product quality</u> The slurry precipitate consisted mainly of $MgSO_3 6H_2O$. Analyses of heavy metals and carbon (assumed to be $MgCO_3$) showed that purities of higher than 98% $MgSO_3 6H_2O$ were obtained with scrubbing slurry pH in the range of 6.5 - 8. Hence CO_2 absorption was insignificant. Casual observations indicated that the slurry precipitate settled very rapidly, could be readily "dewatered", and formed "large" crystals.

(3) MgO utilization per unit SO_2 removed Very little excess MgO was required to achieve the high SO_2 removal efficiencies described above. The maximum found in the three specific tests carried out was 4% above the stoichiometric quantity for formation of magnesium sulphite.

(4) Scrubber operation Despite the small size of the column, no plugging problem was experienced. This could be attributed to both the use of mobile packing and the chemistry of the absorption in the scrubber which produces soluble magnesium bisulphite. It was also found that both the SO_2 removal efficiency and the product quality were quite insensitive to changes in operating conditions. Thus a wide range of conditions could be used, and precise and accurate control is not critical.

(3) Cost Only gross estimates could be made due to the uncertainty in scaling up the present results to commercial operation. However, based on surmised similarities in equipment, in equipment size and in operating conditions, it seems not unreasonable to expect that the capital cost and energy consumption would be favourably comparable to those of the "throw-away" (lime or limestone) process. Based on published data, for a 500 MW power plant utilizing 3.5% - sulphur coal, a selling price (at source) of \$176/t $MgSO_3$ (US\$, 1980) would off-set the direct operating cost. As a comparison, the current US list price (bulk) for epsom salts ($MgSO_4$), used as a fertilizer, is up to \$380/t.

As a secondary objective not directly related to the feasibility assessment, heavy metal contents in the flue gas were estimated. These estimates were based on analyses of the cooling water (270 litres) in the gas quencher, through which a total of more than 3100 Nm^3 of flue gas was passed and spray cooled. Heavy metals such as Co, Cd, Hg, Pb and Sn could not be detected (< 1 ppm). This detection limit corresponds to a conservatively estimated concentration in the flue gas of 0.16 mg/m^3. As a comparison, the emission standards for Pb are in the range of 14 - 46 mg/m^3 as specified by the Alberta Clean Air Act.

The conclusions and recommendations are:

(1) Process feasibility The concept of wet scrubbing of SO_2 gas with MgO for producing potentially saleable products was technically established for application at sour gas plants. High SO_2 removal efficiencies and high product purities could be achieved under favourable operating conditions.

(2) Turbulent contactor This gas-liquid contacting method offers potential advantages over the conventional static packed bed, in terms of gas throughput, pressure drop, plugging and range of operating conditions. Further development at the pilot- or demonstration-scale level is thus warranted.

(3) Market studies These have to be carried out, for specific cases, to better define the potential revenue from the sale of the products. Factors such as demand, market locations relative to the SO_2 emission source, and potential applications that could create new markets should be investigated.

(4) Pilot- or demonstration-scale assessment and development These are warranted and should be carried out (i) to better define the design and operating parameters for scale-up purposes; (ii) to identify potential operating problems; (iii) to obtain better cost estimates; and (iv) to produce sufficient quantities of products for evaluation of their potential applications. The recommended scrubber column size is 460 - 610 mm diameter which would give scale-up factors of 35-20 for full-scale operation at most sour gas plants. The availability of such a unit would also enable other potential users to carry out on-site tests cost-effectively. These would give realistic and site-specific assessment of the system, which could then be used as a sound basis for comparing different options.

(5) Evaluation of other options Evaluation of other process options should be carried out, such as regeneration of MgO and integration of the high concentration of SO_2 into the Claus unit, and production of dry products with a spray dryer by utilizing the heat in the flue gas. Similar tests should also be conducted at other SO_2 emission sources such as oil sands and power plants to evaluate the impurities of the product.

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SOME RELEVANT UNITS OF CONVERSION

Description	To Obtain	Multiply	By
Energy Consumption	BTU/lb	J/kg	2325.8
Liquid Volume	Gallon (Imperial)	Litres	0.22
Liquid Volume	Gallon (USA)	Litres	0.2642
Liquid Flow Rate	USGPM	L/s	15.852
Liquid to Gas Ratio	USG/1000 ACF	L/m^3	7.485
Length	feet	m	3.281
	inches	mm	0.0394
Superficial Velocity	FPM	m/s	196.85
Pressure	inches H_2O at 68°F	kPa	4.01

Temperature conversion:

$$°F = (°C \times 1.8 + 32)$$

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This project was conceived in February, 1983, and its experimental part was completed in November, 1983 - including design and construction of the scrubber system, development of the analytical methods, and on-site tests. The dedication and commitment of those listed as Project Team members certainly played an important role in the successful implementation and completion of this project. However, to accomplish this much over such a relatively short period of time, support and co-operation of others, not formally included as Project Team members, were necessary and indeed received. We wish to gratefully acknowledge their contributions.

Mr. Jack Ondrack, then the President of Baymag Plant, suggested the project. His enthusiasm and optimism provided the much needed initial driving force. Baymag Plant continued its support throughout the project, establishing contacts for potential test sites, providing an engineer for the project and supplying magnesium oxide. The interest, comments and suggestions of Dr. Hagen Schultes, Vice President of Production, were also much appreciated.

The on-site tests were carried out at Gulf Canada's sour gas processing plant in Nevis. As in any on-site project, the support and co-operation of the plant personnel are essential. Mr. John Cooke, Superintendent of the Nevis/Morrin operations of Gulf Canada Resources Inc., and his staff provided us with more than just assistance in man-power and materials. Their enthusiastic and supportive attitude was instrumental in the success of this project. Their contribution in staging the meeting held at the plant on October 21, 1983, and in particular, the genuine interest in and support of the continuation of this project are very gratefully acknowledged.

The Alberta Environmental Centre Management, especially Dr. Malcolm Wilson, Head of the Environmental Technology Wing, provided invaluable guidance and inspiration throughout the project. Not of less importance was his tacit and implicit support.

The encouragement and support of Mr. Paul Layte, Head of the Operations Group and Dr. Albert van Roodselaar, Head of the Pilot Plant Operations, were also important. Their attitude in considering this project as a Wing project, rather than that of a particular individual, Section or Group, was critical to gaining the support and co-operation of all the staff memebers.

Last but not least we wish to acknowledge the cheerful support of the Administrative Support Staff, particularly Barbara Anderson and Connie Gizowski, for preparing this report and for making traveling arrangements during the on-site tests.

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SECTION 1

INTRODUCTION

Acid gases, such as SO_2 and NO_x and to a lesser extent H_2S and HCl, are emitted by many and various industries, including those which are of importance in Alberta. Examples of these emission sources are sour gas, oil sands, power plants, compressor stations and incinerators [1,2,3].

The environmental concerns over these emissions, hence the need for control, and yet at the same time, the economic necessity for selecting cost effective processes are well recognized. In general, the abatement of SO_2 emission is ranked first in terms of both priority and urgency. In a recent report[3], it was stated that additional control measures would have to be implemented to maintain Alberta's total SO_2 emission in year 2000 at the current level.

The assessment, development and transfer of new technologies for pollution abatement are one of the missions of the Alberta Environmental Centre (AEC). It was in fulfillment of this mission that this project was undertaken - to assess and develop new technologies for control of acid gas emissions.

There are a number of control processes in various stages of development. Those in commercial operation are, by far, based on the so-called wet scrubbing processes[4,5,6]. For the purpose of this project, it is convenient to classify these processes into two groups, based on the product of the process:

(1) Throw-away: those which yield products that have no commercial value and hence have to be disposed of. Examples of these are the lime and limestone processes.

(2) Regenerative: those which yield products from which the scrubbing agents could be regenerated and valuable by-products produced. Examples of these are the Wellman-Lord and the MgO processes which produce sulphuric acid as the by-products.

The advantages and disadvantages of these two groups of processes are well known. The throw-away group has lower capital cost and energy consumption but is saddled with disposal problems, which could be not only costly but render it unsuitable in certain locations. The regenerative group eliminates these disposal problems, and derives revenue from the by-product sale, at the expense of higher capital cost and energy consumption.

Conceptually, therefore, the ideal process is one which requires no regeneration, yet produces saleable products. The advantages of both groups are therefore taken, low capital cost and energy consumption without disposal problems, and revenue from the sale of the products.

MgO appears to be a suitable candidate for the scrubbing agent in this concept. The products that could be generated are $Mg(HSO_3)_2$, the pulping chemical in the Magnefite process, $MgSO_3$ and $MgSO_4$ (after oxidation) which have potential applications in the agriculture and construction materials industries. Of not less importance is the fact that a magnesite deposit ($MgCO_3$, a prime raw material for MgO) is available near Alberta and processed in Alberta. Thus, the development of this concept would also represent local resource utilization.

It should be noted that the use of MgO for SO_2 gas scrubbing per se is not a new concept, and its technical feasibility is proven for power plant as well as other applications. The novelty of the above concept, hence this project, lies in the evaluation of the quality and hence the applications and sale value of the products.

The quality of the scrubber products would depend on the emission source and the impurities present. For this reason in particular, the assessment of the above concept must be carried out "on-site". Moreover, at present most technologies in North America have been applied to power plants in the U.S. Differences in emission source and in local conditions thus necessitate the undertaking of this project.

In assessing and developing the above concept the conventional, stage-wise approach was adopted. Laboratory and bench-scale tests would be first carried out to assess process feasibility (in the context of practical applications), followed by pilot- or demonstration-scale tests to define design, operating and scale-up parameters and cost.

This project represented the first stage: the laboratory- and bench-scale tests. It was also limited, in terms of emission source, to the incinerator for Claus tail gas at a sour gas plant. This emission source was selected partly due to the importance of this industry in Alberta and to the likelihood of relatively low contents of impurities.

Finally, it should be noted that wet scrubbing is not the only control process available. Potentially more advantageous but less well developed processes exist, such as spray drying and dry adsorption. Wet scrubbing was chosen first since, being most advanced, it could provide an "immediate solution". Concurrently, exploratory work on these novel concepts is being carried out at the AEC.

SECTION 2

OBJECTIVES AND SCOPE

The objective of this project was to assess the process feasibility of SO_2 gas scrubbing with MgO for producing directly saleable products.

The specific emission source considered was an incinerator for Claus tail gas at a sour gas plant, and the expected results were information on SO_2 removal efficiency, purity of the scrubbing products, effectiveness of MgO utilization, and preliminary cost estimates.

The scope of this project included the following:

(1) design, construction, and on-site assembly and operation of a bench-scale wet scrubbing system
(2) scrubbing of a slip stream of the incinerator flue gas
(3) measurements of:
    (i) variation in SO_2 removal efficiency and the corresponding pressure drop with pH of the scrubbing slurry, liquid/gas flow ratio, and superficial gas velocity through the scrubber.
    (ii) characteristics and purity of the scrubber products.
    (iii) utilization of MgO, in terms of Mg usage per unit SO_2 removed.
(4) observations on plugging and on ease of control and operation.

As a secondary objective, the contents of impurities in the flue gas, such as heavy metals, would also be estimated.

SECTION 3

PROCESS DESCRIPTION

Figure 3.1 is a schematic diagram of the process, showing the "slaking" of MgO, the addition of the resulting slurry into the regeneration tank (R), the absorption of SO_2 gas in the scrubber (A), and the products that could be obtained: $MgSO_3 \times H_2O$ from the regeneration tank and $Mg(HSO_3)_2$ from the scrubber outlet.

The overall reactions could thus be represented by

$$MgO + SO_2 + xH_2O \rightarrow MgSO_3 \times H_2O \quad (3.1)$$

or $$MgO + 2SO_2 + H_2O \rightarrow Mg(HSO_3)_2 \quad (3.2)$$

These overall reactions do not represent the mechanisms by which MgO is utilized to remove SO_2. In fact, it is $MgSO_3$, and not MgO, which is the active scrubbing agent. The simplified mechanisms can be described by the following reactions:

(1) MgO slaking

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad (3.3)$$

(2) Absorption in scrubber

(i) Physical dissolution of SO_2 gas

$$H_2O + SO_2 \rightarrow H_2SO_3 \quad (3.4)$$

(ii) Chemical reaction

$$MgSO_3 + H_2SO_3 \rightarrow Mg(HSO_3)_2 \quad (3.5)$$

(3) $MgSO_3$ regeneration

$$Mg(OH)_2 + Mg(HSO_3)_2 \rightarrow 2MgSO_3 + 2H_2O \quad (3.6)$$

(4) Hydration and precipitation

$$MgSO_3 + xH_2O \rightleftarrows MgSO_3 \times H_2O \quad (3.7)$$

The following comments on the above mechanisms should be noted:

(1) Relationship to overall reactions The overall reactions (3.1) and (3.2) could be arrived at by appropriately combining Reactions (3.3) to (3.7). An operation resulting in Reaction (3.1) means that all the $Mg(HSO_3)_2$ produced in the scrubber (Reaction (3.5)) is converted to $MgSO_3$ in the regeneration tank, which is then partly recirculated and partly withdrawn as the scrubber product. Reaction (3.2) means that $MgSO_3$ is recirculated within the system, and the $Mg(HSO_3)_2$ produced is partially withdrawn as the product, with the remaining used to regenerate the recirculated $MgSO_3$.

(2) Rationale for use of $MgSO_3$ as the active agent It is well known and experimentally verified (Appendix I) that $MgSO_3$ reacts with dissolved SO_2 at a faster rate than does $Mg(OH)_2$. Thus, it would not be desirable to introduce the latter directly into the scrubber. Moreover, the reaction product of the $MgSO_3$ reaction is $Mg(HSO_3)_2$, which is highly water-soluble. Hence, plugging tendencies in the scrubber would be reduced.

(3) $MgSO_3$ regeneration To ensure sufficient $MgSO_3$ and to minimize the less reactive $Mg(OH)_2$ in the recirculated scrubbing slurry, the regeneration tank should be sized for sufficient residence time to "complete" Reaction (3.6). This is desirable, not only for efficient absorption in the scrubber, but also to minimize the quantity of $Mg(OH)_2$ in the scrubber product, which is an "impurity" in the process being assessed.

Preliminary laboratory tests indicated that a residence time of 10 minutes is adequate (Appendix II). This was also verified during the field operation.

(4) Side reactions Since flue gases contain CO_2, O_2 and in some cases NO_x, side reactions could also take place in the scrubber. These could give rise to the formation of carbonate, nitrate and sulphate salts. The carbonate salts in particular are of concern because of the relatively high CO_2 content in the tail gas compared to SO_2, and also since they represent impurities in the product.

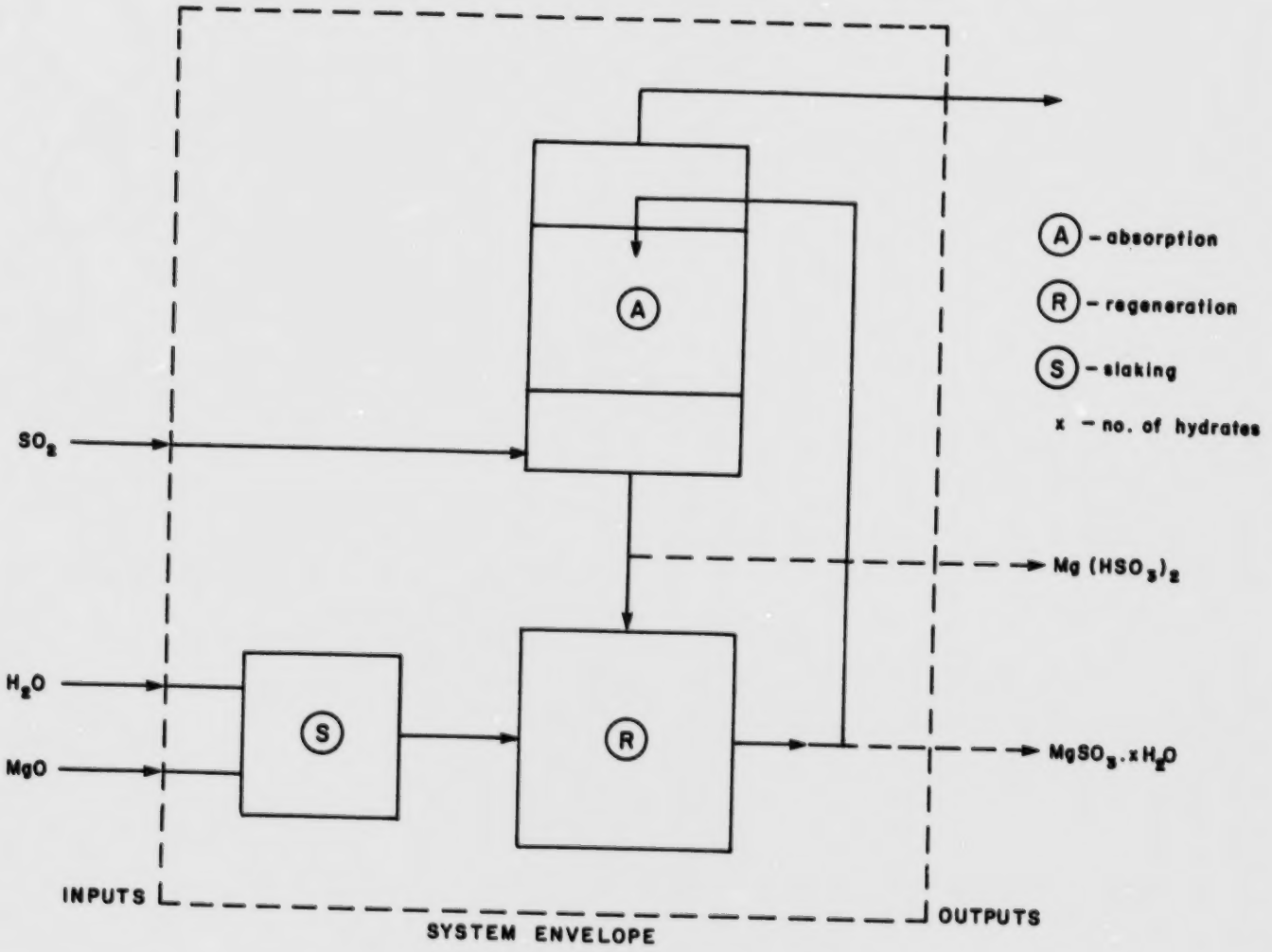


FIGURE 3.1 . SCHEMATIC OF MgO - BASED WET SCRUBBING .

SECTION 4

EQUIPMENT, OPERATION AND MATERIALS

4.1 Emission Source

Figure 4.1 shows a simplified flow diagram of a typical sour gas processing plant. The sulfur recovery in the Claus Reactor is limited by a combination of equilibrium and kinetic factors. Hence, Claus tail gas contains unreacted hydrogen sulfide, sulfur dioxide and entrained sulfur. Small amounts of carbonyl sulfide and carbondisulfide may also be present. This tail gas is then incinerated to convert all the sulfur compounds to sulfur dioxide.

The present gas plant has two tail gas incinerators (Figure 4.2) connected to a common stack. A small slip stream (approximately 0.007 Nm^3/s) from one of the incinerator outlets was withdrawn and introduced into the scrubber system, and the scrubbed gas was then returned to the air intake of the second incinerator. This eliminated the discharge of the scrubber outlet gas to the immediate surroundings, and hence safety concerns during non-optimum operation of the scrubber system.

Typical gas composition at location (A) in Figure 4.2 is shown in Table 4.1.

Since the inlet tail gas quality and quantity differ for the two incinerators, the gas composition of the slip stream (location (B)) is not necessarily the same as that given in Table 4.1. The gas composition measured at the scrubber inlet during the test period is given in Table 4.2.

4.2 Scrubber System

Figure 4.3 is a schematic diagram of the scrubber system, showing its main components and operation. This system was designed to facilitate dismantling, hence transport, and on-site re-assembly at the test location.

With reference to Figure 4.3, the main components of the system and the operation can be described as follows:

4.2.1 Gas Passage

An induced draft (ID) fan (A) was used to withdraw the flue gas from the incinerator via a hot flue gas pipe (B), a gas quencher (C), through the scrubber columns (D) and a cyclone (E), then to discharge the scrubbed gas via an exhaust pipe (F) to the intake of the second incinerator. The gas flow through the scrubber columns was controlled by a damper control valve (G) and measured using an orifice plate (H).

The hot flue gas pipe was 316 SS (Stainless Steel), 51 mm diameter, 4.5 m long, and uninsulated to reduce the heat load on the quencher. (A temperature drop from about 480°C to 200°C was obtained). The quencher consisted of a 76 mm diameter, 2.4 m long spray tower immersed in a 270 litres reservoir tank. Cooling water was recirculated from the tank and sprayed from the top of the tower in a closed cycle operation. (Throughout the tests, no nozzle plugging was experienced, thus indicating minimum particulate loading in the flue gas.) This closed cycle operation was used to minimize SO_2 absorption in the quencher. It was found that the pH of the recirculated water reached 1.5 to 2.0 and no SO_2 absorption was observed.

Two safety features were incorporated. The first was an additional spray nozzle, connected to a main water supply, which would be activated when the temperature of the quencher exit gas reached 93°C. The second was a relay that would shut off the ID fan if this temperature reached 120°C.

Two identical scrubber columns, arranged in parallel to double the gas throughput, were used. These were 51 mm diameter, 1.2 m long pyrex glass columns in 0.6 m long sections. (Glass was used to facilitate observations on plugging, channelling and liquid-gas mixing). In each column, liquid-gas contact was effected counter currently in a two-stage turbulent bed contactor. In brief, each stage consisted of 9.5 mm diameter hollow polypropylene spheres (bulk specific gravity 0.2, static depth 51 mm), placed between two retaining grids with 610 mm separation. (This arrangement results in turbulent and random motion of the spheres, thereby promoting intimate gas-liquid contact and minimizing plugging and liquid chanelling. Additional advantages over the conventional static packed bed are less susceptibility to flooding, thereby increasing the operating range, and relatively lower pressure drops [7,8].)

The cyclone was a 102 mm diameter glass cyclone, used to collect condensed and entrained water droplets. The ID fan was a constant speed, 0.25 kw fan, capable of withdrawing 0.01 Nm^3/s at 6.2 kPa vacuum. The exhaust pipe was made of 51 mm diameter steel pipe.

4.2.2 Slurry Passage

The scrubbing slurry was recirculated from the regeneration tank (I) to the top of the scrubber columns (D) with peristaltic pumps (J); flowed down by gravity through the columns, coming into contact with the up-flowing gas; entered a small cylindrical vessel (L), where its pH was measured; then overflowed onto an attached outer tray, where the $Mg(OH)_2$ slurry was added, and finally returned to the regeneration tank.

The make-up $Mg(OH)_2$ was prepared about 24 hours in advance by slaking MgO in hot water. It was contained in a 100 litre tank (K), continuously stirred, and delivered to the outer tray of vessel (L) by a peristaltic pump (M). The flow rate of the $Mg(OH)_2$ slurry was controlled manually based on the desired pH in the regeneration tank.

The regeneration tank was equipped with a stirrer and the volume of slurry in it was maintained to give a minimum liquid residence time of 15 minutes. Periodically, the precipitate in tank was removed to control the slurry concentration.

The scrubbing slurry was fed into each scrubber column via an open pipe of 13 mm diameter. Despite the absence of a liquid distributor, no channelling was observed, thus confirming the advantage of the turbulent bed contactor.

4.2.3 Sampling Points

For the gas, the major sampling points were before the quencher, and before and after the scrubber columns. These were used for measurements of temperature and pressure and for withdrawal of samples for gas analysis (see next section). Differential pressures across the scrubber columns and the orifice were also measured.

Temperature and pH were measured in vessel (L) for the scrubber outlet and in the regeneration tank for the scrubbing slurry. This latter pH was continuously recorded on a strip chart recorder.

4.2.4 Gas Sampling/Analysis

Figure 4.4 is a schematic diagram of the gas sampling/analysis system. It consisted of heat-traced, 6 mm diameter teflon tubing (A), connecting the sampling points to the selector valves (B); a heated box containing filters (C) for particulate removal, and a permeation dryer (D) for specific and selective moisture removal [9,10]. This sampling system was designed to prevent condensation and loss of the gases to be analysed.

After drying, the gas sample entered a variable, mass flow controlled dilution system capable of up to 5000 dilution ratios. This approach was used to allow the use of one set of analysers for both the scrubber inlet and outlet.

The gas analysers were: Monitor Labs, fluorescent SO_2 analyser (Model 8850); Infrared Industries, Coulometric O_2 analyser (Model 2100) and Infrared Industries, Infrared CO_2 analyser (Model 703D).

Premixed gases in cylinders were used as standards for calibration. These standards were introduced at various locations in the sampling system to determine losses in the sampling line. In addition, the SO_2 analyser was calibrated using a permeation tube standard, and periodically, verification was carried out using "wet chemical" methods (Orsat and Impinger sampling train).

4.2.5 Auxiliary Equipment

A 3 m x 4.9 m trailer, located adjacent to the scrubber system was used to house the gas analysers, the dilution system, strip chart recorders, and miscellaneous "wet chemical" equipment, as well as serving as an office.

4.2.6 Magnesium Oxide

The MgO used in this project was supplied by Baymag Plant. It was calcined magnesite from the Rocky Mountains, the composition of which is shown in Table 4.3.

TABLE 4.1: GAS COMPOSITION (*) AT LOCATION (A) IN FIGURE 4.2

COMPONENT	CONCENTRATION (%, dry basis)
CO_2	14.73
SO_2	0.43
O_2	9.22
N_2	75.62

(*) Source: Stack Emission Survey Results - Gulf Canada Resources, Nevis

TABLE 4.2: MEASURED GAS COMPOSITION AT LOCATION (B), FIGURE 4.2

Temperature : 400°C to 482°C

COMPONENT	CONCENTRATION RANGE (%, dry basis)
CO_2	12 - 29
SO_2	0.33 - 1.26
O_2	7.0 - 9.5

TABLE 4.3: PROPERTIES OF MgO(*)

1. Chemical Composition

COMPONENT	CONCENTRATION % loss free basis
MgO	97.0
CaO	1.6
Fe_2O_3	0.7
Al_2O_3	0.1
Acid Insolubles	0.4

2.	Loss on Ignition	1 - 2%
3.	Sieve Analysis	95% passing through 200 mesh
4.	Bulk Density	0.6 - 0.8 kg/L (37 - 50 lbs./ft^3)

(*) Source: Baymag Plant Data Sheet, Baymag 30

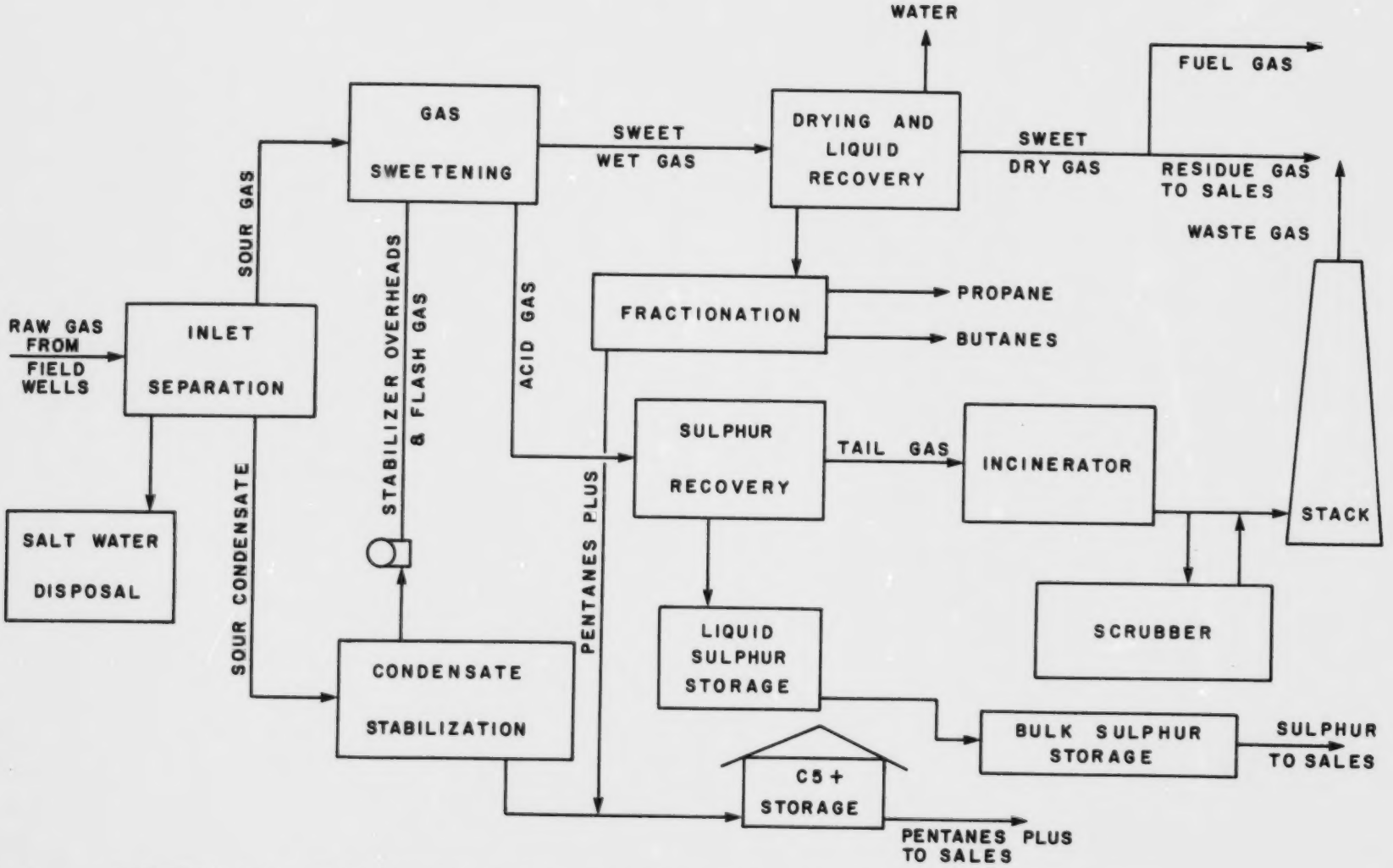


FIGURE 4.1 .SIMPLIFIED FLOW DIAGRAM OF GAS PROCESSING PLANT .
(Reference no. 16)

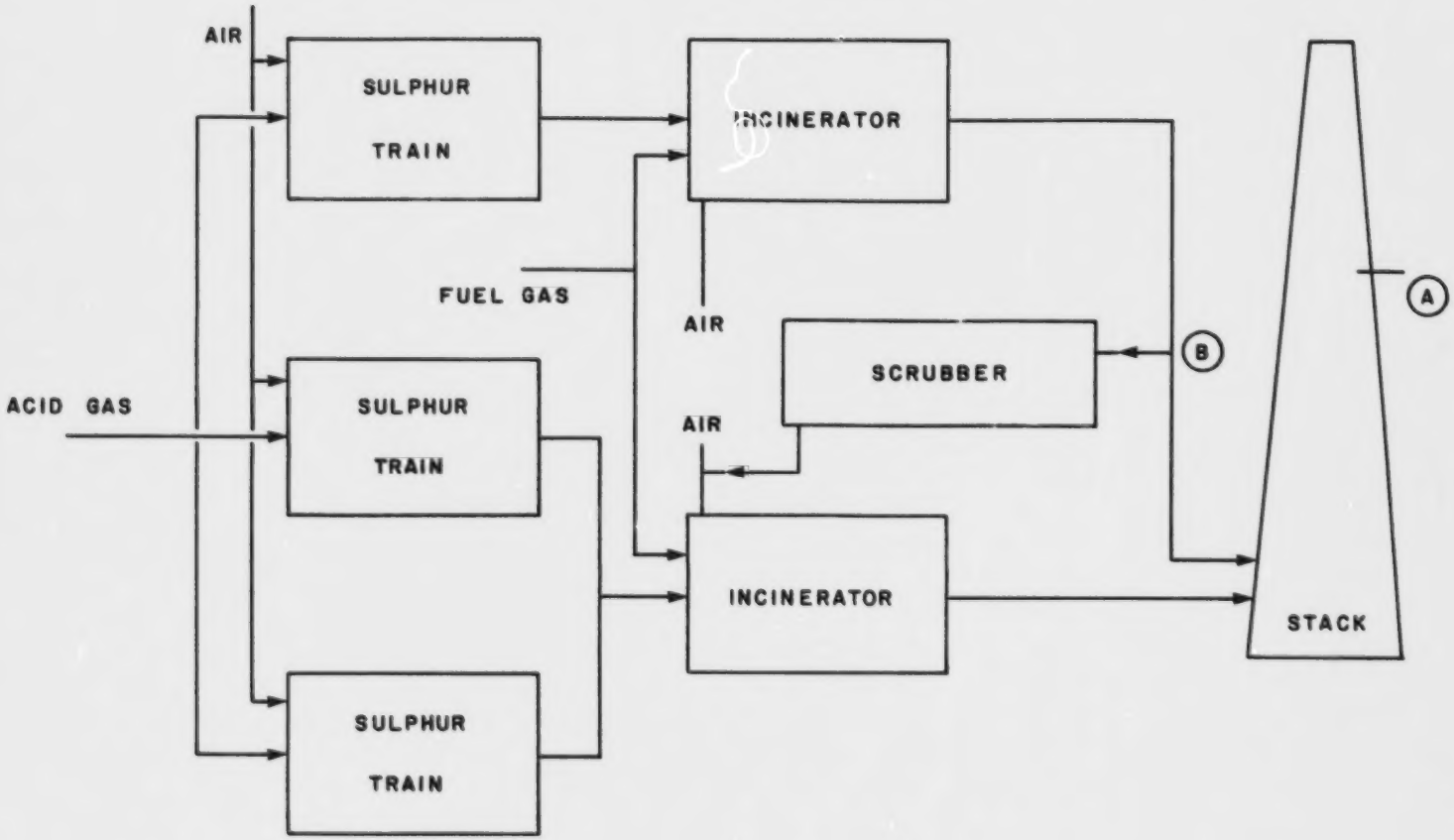


FIGURE 4.2 . SCHEMATIC DIAGRAM OF THE GAS PLANT SHOWING SCRUBBER SYSTEM LOCATION .

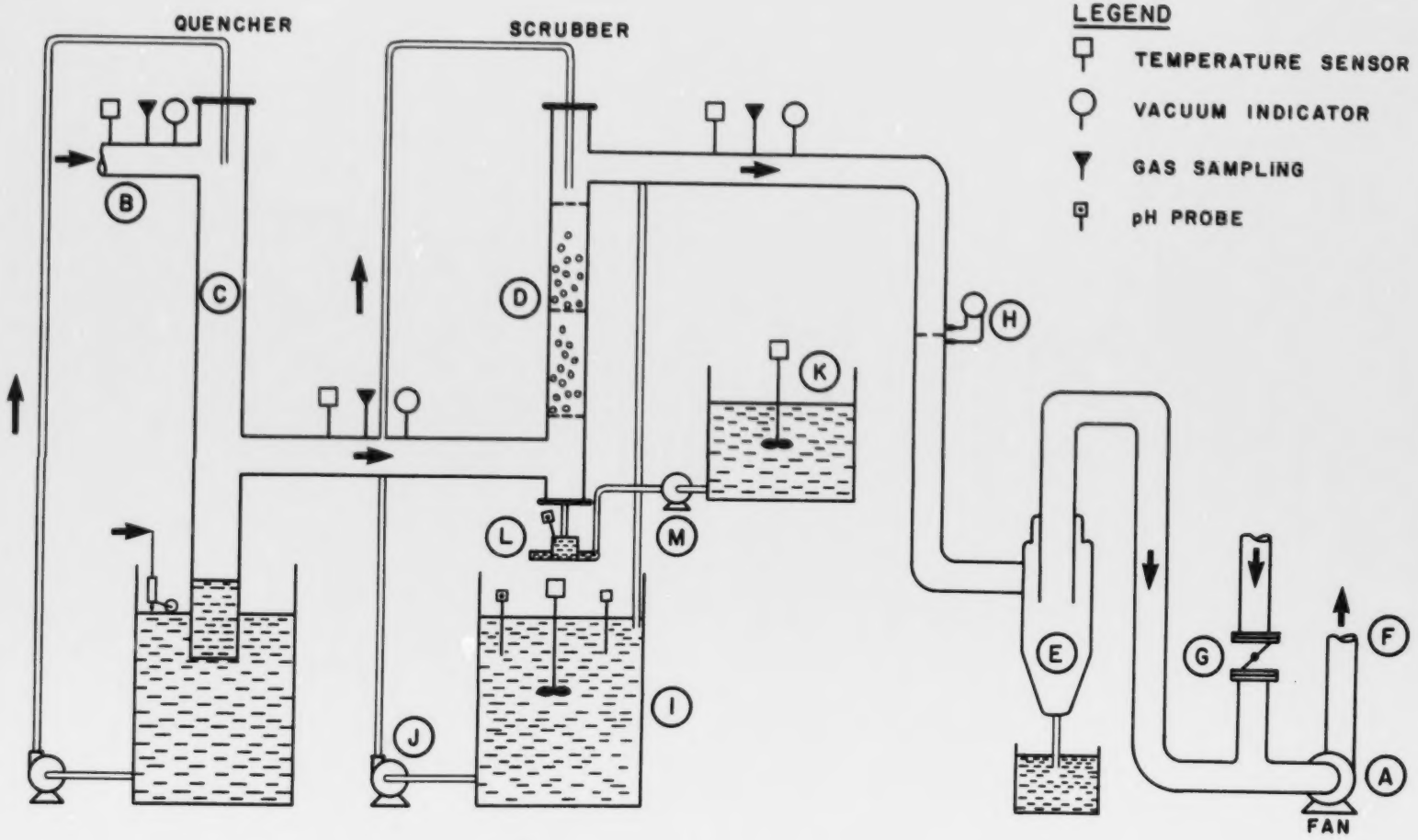


FIGURE 4.3 . SCHEMATIC DIAGRAM OF BENCH-SCALE SCRUBBER SYSTEM .

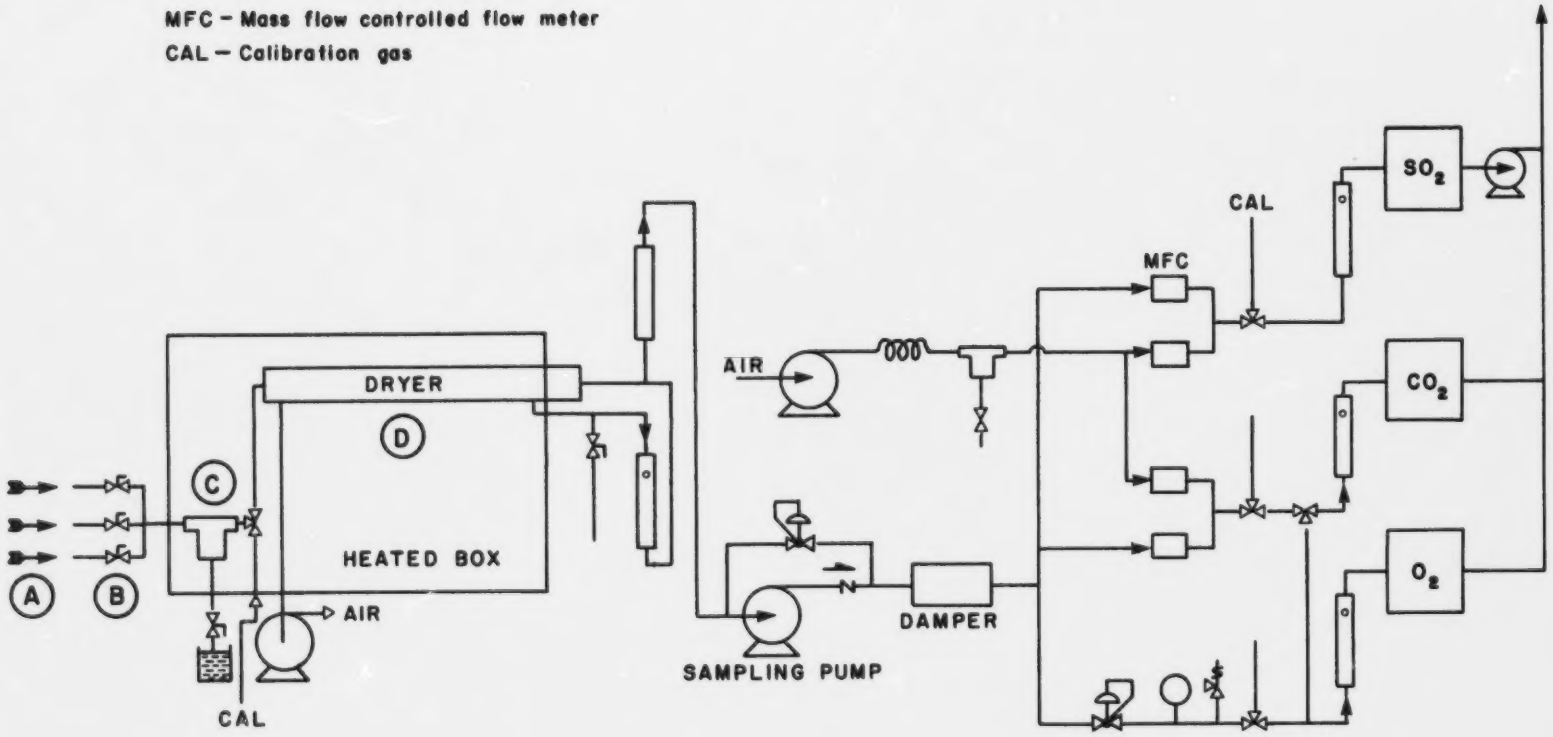


FIGURE 4.4 . GAS SAMPLING AND ANALYSIS SYSTEM .

SECTION 5

RESULTS AND DISCUSSION

5.1 Initial Design and Operation

From the onset it was apparent that, due to the small size of the scrubber columns, plugging would be a potential problem. It was decided therefore to use a mobile, turbulent contactor rather than the conventional static packed bed. The scrubber system was then set up at the AEC, prior to the on-site testing, and preliminary tests were carried out to determine the appropriate scrubber column configuration and ranges of operating conditions. Additional preliminary tests were also carried out on-site for confirmation.

The criteria for selection were based on those operating conditions found in commercial systems. These were: SO_2 removal efficiency higher than 90%, column pressure drop lower than 2.5 kPa, gas velocity through the column higher than 2 m/s, liquid to gas flow ratio higher than 2.6 L/m^3 and stable operation.

The results of the preliminary tests were the following:

(1) Configuration of turbulent contactor A static height of 51 mm and a freeboard height of 610 mm (distance between retaining grids) were found to produce stable operation with gas velocities up to 3.6 m/s and liquid/gas ratios of up to 6.7 L/m^3.

(2) Number of stages A two-stage column was found adequate to remove up to 15,000 ppm SO_2 with efficiencies higher than 95% and column pressure drops lower than 2.5 kPa.

(3) Scrubbing slurry concentration The minimum concentration as dictated by stoichiometric requirements for complete removal can be computed to be:

$$c = 6.3\ a/(L/G)$$

where c = concentration of $MgSO_3 6H_2O$ in the scrubbing slurry, in wt. %
a = inlet SO_2 concentration in vol. %
L/G = liquid/gas ratio in L/m^3

Thus, for an inlet SO_2 concentration of 1%, and a liquid/gas ratio of 2.6 L/m^3, the stoichiometric slurry concentration would be about 2.5%. It was therefore pleasantly surprising to find that 2 - 3% slurry was adequate to achieve SO_2 removal efficiencies higher than 95%. This suggested adequate liquid-gas contact, and hence reaction rate was not the dominant or controlling factor.

The feasibility of using slurry concentrations close to the stoichiometric requirements (hence relatively dilute) is advantageous. In this project, slurry concentration did not need to be considered as a variable. More importantly, in commercial operation, the pumping requirements are less severe and potential plugging in the transfer line is minimized.

(4) Superficial gas velocity Superficial gas velocity is an important design and operating variable, related to both capital and operating costs. It represents a direct measure of the gas throughput capacity per unit cross-sectional area of the scrubber column, and affects the pressure drop across the scrubber column.

However, since scale-up parameters could not be confidently derived from the presently used small system, no attempt was made to "optimize" this variable. The preliminary tests carried out were aimed at determining the variation in SO_2 removal efficiency within the typical range of gas velocities found in commercial operation.

Figure 5.1 is a summary of the results, showing the small variation in SO_2 removal efficiency with gas velocities in the range of 2 - 3 m/s and L/G in the range of 1.3 to 4.7 L/m^3, with scrubbing slurry pH of 8 - 9 and concentration of about 3%. Hence, high efficiencies could be achieved over a wide range of operating conditions. For most of the tests, a gas velocity of 2.5 m/s was used.

5.2 SO_2 Removal Efficiency

In the preliminary tests, it had been established that SO_2 removal efficiencies higher than 95% could be achieved over a wide range of operating conditions. Subsequent more detailed tests were carried out to determine the effect of pH of the scrubbing slurry and L/G ratio.

The significance of these variables includes:

(1) Selective or preferential absorption of SO_2 over CO_2 could be effected by lowering the scrubbing slurry pH, thereby increasing the purity of the scrubber products and reducing the MgO usage per unit SO_2 removed.

(2) The scrubbing slurry pH and L/G determine the availability of $MgSO_3$ for absorbing SO_2. This pH affects the ratio of $MgSO_3/Mg(HSO_3)_2$, as shown in Figure 5.2, and the L/G is a direct measure of the ratio of available $MgSO_3$ to SO_2 to be scrubbed.

(3) Pumping costs for both the gas and the slurry are directly related to scrubber column pressure drop and slurry flow rate, which in turn, are affected by L/G.

The results are summarized in Figure 5.3, showing that SO_2 removal efficiencies higher than 95% were obtained for pH $\geq$ 5.5 and L/G $\geq$ 2 L/m^3. The insensitivity to pH is particularly significant since this means that pH control is not critical, and more importantly, the absorption of CO_2 can be minimized. The results with respect to L/G are also encouraging in that L/G = 2.7 L/m^3 is typically considered a low value in commercial operation. Hence, pumping costs should be favourable.

The low efficiencies obtained for pH = 5 and L/G = 2 L/m^3 could be attributed to two possible factors:

(1) There was insufficient quantity of $MgSO_3$ to meet the stoichiometric requirements, or

(2) There was insufficient liquid-gas contact to "complete" the SO_2 absorption reaction.

Based on the observed variation with pH at L/G = 2 L/m^3, stoichiometric calculations, and little variation in liquid hold-up with L/G (Appendix III), it was surmised that the first factor was predominant. That is, provided that the stoichiometric requirement for $MgSO_3$ was met, SO_2 removal efficiencies higher than 95% would be obtained.

5.3 Scrubber Column Pressure Drop

The variation in total scrubber column pressure drop with L/G is shown in Figure 5.4. Combining these results and those given in Figure 5.3 shows that an SO_2 removal efficiency of 95% could be achieved with a pressure drop of 1.5 kPa.

Although the present results could not be scaled up to commercial operation with great confidence, the results are nevertheless very encouraging. A pressure drop of 1.5 kPa is considered typically low. Hence, the power requirement for gas transport, which is a major operating cost, is favourably low.

5.4 Scrubber Product Characterization

5.4.1 Approach

The characteristics of the precipitate in the regeneration tank, ideally $MgSO_3 \times H_2O$, were used as an indication of the scrubber product quality. This precipitate was thus produced and analysed for $MgSO_3$, x (hydrate form) and other compounds that might be present as a result of absorption of CO_2 and other impurities in the flue gas.

Since CO_2 absorption was of main concern, and since this absorption would be affected by the scrubbing slurry pH, a number of tests were carried out at different values of scrubbing slurry pH. In each test, the operating conditions were maintained steady, and the SO_2 removal efficiency was kept higher than 95%. The test duration was sufficiently long (4 - 11 hours) to minimize possible effect of fluctuations in inlet gas quality and to produce sufficient quantity of precipitate for analysis and for future evaluation of product applications.

5.4.2 Operating Conditions

The operating conditions under which the precipitates were produced were:

- Scrubbing slurry pH = 6.5 - 8.0
- L/G = 2.7 L/m^3
- Superficial velocity = 2.5 m/s
- Inlet SO_2 concentrations = 3000 - 10,000 ppm
- SO_2 removal efficiency > 95%

5.4.3 Analytical Methods

(1) "Free water" was removed by drying to constant weight at 65°C, at which H_2O associated with hydration would still be retained.

(2) Weight loss resulting from heating at 220°C in an oven and Thermogravimetric Analysis (TGA) were used to determine the hydrate form. The latter was also used to measure weight loss upon heating in N_2 atmosphere, up to 750°C.

(3) Inductively Coupled Plasma (ICP) Atomic Emission Spectroscopy was used to measure Mg, Ca, Fe and S (see Appendix IV).

(4) A Beckman Carbon Analyser, Tocamaster 915B, was used to measure C (see Appendix IV).

5.4.4. Chemical Composition

Table 5.1 is a summary of the analyses of precipitate samples heated at 220°C, showing the Mg and S contents and the difference between these and the computed values based on $MgSO_3$.

Thus, these results strongly suggest that $MgSO_3$ was the main compound in the samples. Further corroborating evidence was provided by:

(1) Results of ICP analyses for Ca, Fe, Mn and other heavy metals, and carbon analysis, showing impurities of less than 2% wt (carbon assumed to be $MgCO_3$).

(2) TGA results, showing weight losses of 58-60% upon heating from 250°C to 700°C (see sample results in Figure 5.5). These values are in agreement with that associated with loss of SO_2 from $MgSO_3$ (61.5%). Furthermore, the weight loss occurred in the temperature range of $MgSO_3$ decomposition [11].

5.4.5 Hydrate Form

There are two possible hydrate forms, $MgSO_3$ $3H_2O$ and $MgSO_3$ $6H_2O$, that is, x=3 and x=6. Based on the TGA results on the weight loss of samples (dried at 65°C) upon heating from room temperature to 250°C, the computed values of x ranged from 5.1 to 5.3 (see Figure 5.5). Additional data were also used to determine the value of x. These were the Mg contents in samples dried at 65°C and at 220°C. The computed values of x ranged from 5.0 to 6.2 (average = 5.5, standard deviation = 0.37, 10 samples).

The results strongly suggest therefore that the precipitate was mainly $MgSO_3$ $6H_2O$. The computed values of x that were less than 6 could be attributed to partial loss of hydrate upon heating at 65°C. It should also be noted that the dehydration temperatures are 70-100°C for x=6 and 120-200°C for x=3 [12]. Thus, the TGA results, showing that most of the weight loss occurred below 150°C, are further corroborating evidence.

Additionally, it may be noted that the nature of the hydrate formation depend somewhat on the temperature in the scrubber regeneration tank. Figure 5.6 shows the temperature stability of $MgSO_3$ - H_2O System [13]. Since the regeneration tank temperature was in the range of 20°C to 45°C during the present study, formation of hexahydrates is not unexpected.

5.4.6 Settling Characteristics

No quantitative measurement was made. However, casual observations indicated that the precipates settled very rapidly, could be readily dewatered and formed "large" crystals. These properties are consistent with the reported

properties of $MgSO_3$ $6H_2O$. This is significant in that these properties facilitate further treatment of the slurry, such as clarification, filtration and centrifugal separation.

5.5 MgO utilization

From the finding that the precipitate in the regeneration tank was mainly (98%+) $MgSO_3$ $6H_2O$, it could be deduced that the MgO utilization would be close to stoichiometric requirements. That is, there was very little MgO unutilized or used to absorb CO_2. As a confirmation, additional tests were carried out.

In each test, the scrubber operation was brought to and then maintained at steady state conditions. At the beginning and at the end of the steady state run, the quantity of slurry in the regeneration tank was noted and samples were taken for Mg and S analyses. For convenience, and to minimize the number of analyses to be carried out, the scrubber was operated in a closed operation (that is, no bleed was taken out). Thus, the measured increases in Mg and in S in the regeneration tank could be used to compute the MgO usage per unit SO_2 removed.

The results are summarized in Table 5.2. Note that the stoichiometric Mg/S weight ratios are 0.75 and 0.375 for $MgSO_3$ and $Mg(HSO_3)_2$, respectively, corresponding to atomic ratios of 1/1 and 1/2. The results, showing ($\Delta Mg/\Delta S$) weight ratios of 0.70 and 0.67, thus confirm the previous finding that all the MgO introduced into the system was utilized for SO_2 removal. Note that, as expected, $Mg(HSO_3)_2$ would be present in the liquid portion of the slurry in the regeneration tank. Thus, values of ($\Delta Mg/\Delta S$) ratio considerably less than 0.75 were found in this liquid portion, thereby resulting in overall ($\Delta Mg/\Delta S$) ratios of less than 0.75.

An additional test was also carried out at AEC, under better controlled conditions, to "balance" the quantities of Mg and S added (i.e. MgO and SO_2) and the corresponding increases found in the regeneration tank.

Here, the flue gas was simulated by heating compressed air to 200°C and injecting desired quantities of CO_2 and SO_2 gas from compressed gas cylinders.

The results are summarized in Table 5.3, confirming the on-site test results. Note also that reasonable agreement was obtained in the Mg and S "mass balance".

5.6 Heavy Metal Impurities in the Flue Gas

The gas quencher was operated as a closed system in that the cooling water was not replaced throughout the project, during which a total of more than 3100 Nm^3 of incinerator flue gas was spray cooled. Since only about 270 litres of cooling water was used, analyses of heavy metals in it would provide a sensitive means of detection and estimation of their quantities in the incinerator flue gas.

ICP scans were carried out on the quencher cooling water (towards the end of the project) and on grab samples of the plant water. The results are summarized in Table 5.4.

There are a number of confounding factors which make it difficult to estimate the quantities of these metals in the incinerator flue gas. For example, the presence of Si, Mn, Cr, Ni, Mo and Fe could be accounted for by corrosion of the 316 SS quencher pipe used, which came into contact with the acidic cooling water (pH = 1.5-2). Table 5.5 shows their estimated concentrations, based on published data on the corrosion rate [14].

Nevertheless, it is interesting to note the results for those metals which are neither associated with stainless steel nor present in the plant water. For a 100% collection efficiency in the quencher, the detection limit of 1 ppm corresponds to about 0.08 mg/m^3 in the incinerator flue gas. Thus, based on a conservative assumption of 50% collection efficiency, the concentrations of heavy metals such as Co, Cd, Hg, Pb and Sn, since they were not detected, would be less than 0.16 mg/m^3. The significance of this value can be appreciated by comparing it to the allowable emission standard for Pb, which is in the range of 14-46 mg/m^3 as specified by the Alberta Clean Air Act.

5.7 Cost Estimates: Comparison With Existing Wet Scrubbing Processes

Accurate estimation of capital and operating costs was beyond the scope of this project. The small size of the test equipment would not warrant the scaling up of the results to commercial operation. Nevertheless, it seems not unreasonable to surmise that the capital and operating costs of SO_2 removal would not exceed those for the lime or limestone process (excluding chemical cost). This conjecture is based on the following:

(1) Similar equipment could likely be used, and no additional equipment is required. Also, the superficial gas velocities used, in the range of 2 - 3 m/s are within and on the higher side of those found in commercial operation. Hence, equipment size should also be similar and could be smaller.

(2) The relatively low values of pressure drop (1.5 kPa), L/G (2.7 L/m^3) and slurry concentration (2-3%) could, in fact, result in lower gas and slurry pumping costs.

(3) The favourable settling and dewatering characteristics of the slurry could also result in a reduction in slurry treatment cost (e.g. filtering, clarification and centrifugal separation).

An overall, gross comparison with the throw-away and the regenerative processes can thus be made, as summarized in Table 5.6. There is an increase in operating cost due to the "one-pass", as opposed to recycled, usage of MgO, which is more costly than lime (assumed difference $220/t). However, this is off-set by the lower capital cost and energy consumption compared to the regenerative process, and the absence of disposal costs of the throw-away process.

The main economic advantage lies, however, on the sale of the scrubber product. In terms of recovering the total operating cost, the break-even, at-source selling price is about $176/t $MgSO_3$ for a 500 MW, 3.5% - sulphur coal power plant. This can be compared with the current US list price of up to $380/t for epsom salts ($MgSO_4$) used as a fertilizer [15].

The economics of the process would, however, depend also on other factors, such as market availability and proximity to the emission source. Further work is thus still required. Moreover, better estimates of capital and operating costs should be obtained. As elaborated in Appendix V, these costs vary markedly and are heavily dependent on site-specific conditions. Hence it would be difficult to obtain reliable cost estimates for a particular application at a specific location.

It is our contention, therefore, that on-site pilot plant testing is necessary for further economic and technical assessment.

5.8 Alternatives

Even if the scrubber product quality, value and demand are favourable, the economic viability of this concept is still site-specific. For example, at locations remote from either the MgO source or the product market, the transportation costs could be prohibitively high. In such cases, it could be more economically viable to consider the regeneration of MgO and the production of SO_2. The resulting concentrated SO_2 could either be recycled to the Claus plant or used for manufacturing sulphuric acid. The latter is particularly attractive if sulphuric acid is used elsewhere in the plant.

Another means of reducing transportation cost is the production of dry scrubber products by utilizing the "waste heat" in the flue gas. This could be achieved by spray drying/scrubbing. This relatively novel technology has additional advantages, such as low operating cost and minimum slurry after-treatment (e.g. clarification, filtering or centrifugal dewatering).

In summary, assessment of other options at different site-specific locations needs to be carried out.

TABLE 5.1: Mg AND S ANALYSES OF PRECIPITATE SAMPLES HEATED AT 220°C

Test Date (1983)	Scrubbing Slurry pH	Mg wt %	ΔMg(1) %	S wt %	ΔS(1) %
Sept. 15	8.0	24.8	1.5	23.8	-6.9
Sept. 16	8.0	23.0	-0.3	30.7	0.0
Sept. 19	8.0	21.4	-1.9	28.0	-2.7
Sept. 20	7.5	23.0	-0.3	29.6	-1.1
Sept. 21	7.5	24.1	0.8	30.2	-0.5
Sept. 22	7.2	22.9	-0.4	29.3	-1.4
Sept. 23	7.5	24.6	1.3	28.2	-2.5
Sept. 26	7.5	25.1	1.8	28.3	-2.4
Sept. 28	7.7	27.4	4.1	n/a	-
Oct. 4	6.5	24.6	1.3	n/a	-

(1) ΔMg = (Mg - 23.3) %, where 23.3% is the Mg content in $MgSO_3$

ΔS = (S - 30.7) %, where 30.7% is the S content in $MgSO_3$

n/a not analysed

TABLE 5.2: MgO UTILIZATION ON-SITE TEST RESULTS

DATE (1983)	DURATION OF TEST seconds x 10^3	REGENERATION TANK pH	SO_2 REMOVAL EFFICIENCY (%)	ΔMg/ΔS PRECIPITATE	LIQUID	OVERALL
Sept. 28	16.26	7.7	97.2	0.72	0.46	0.70
Nov. 2	19.2	6.5	95.5	0.76	0.56	0.67

NOTES:
- Pressure drop = 1.5 kPa; L/G = 2.4 L/m^3.
- Gas velocity 2.5 m/s
- ΔMg/ΔS: ratio of the increase in Mg in the regeneration tank to that in S.

TABLE 5.3: "MASS BALANCE" AND MgO UTILIZATION TEST RESULTS AT AEC

1) Measured quantities and consistency

ELEMENT	INPUT (g)	OUTPUT[a] (g)	AVERAGE (g)	DIFFERENCE %
Mg	650	690	670	3
S	900[b]	810	855	5

(a) Accumulated in regeneration tank

(b) Net Input = Difference between the contents in inlet and outlet gas

2) MgO Utilization

Mg/S = 0.78

TABLE 5.4: CONCENTRATIONS OF METALS

METAL	CONCENTRATION, ppm in PLANT WATER [a]	QUENCHER WATER [b]
Mg	20	80
Ca	80	25
Fe	(nd)	500
Mn	(nd)	5
Si	5	40
Cu	(nd)	5
Zn	(nd)	10
Cr	(nd)	100
Ni	(nd)	20
B	(nd)	1
Misc [c]	(nd)	(nd)

(a) Grab Sample

(b) Sampled on October 7, 1983 (total flue gas = 3100 Nm^3; vol. quencher water = 270 litres)

(c) Co, Cd, Hg, Pb and Sn

(nd) Below detection limit of about 1 ppm

TABLE 5.5: ESTIMATED RANGES OF METAL CONCENTRATIONS DUE TO CORROSION OF 316 SS QUENCHER PIPE

Metal	Range, ppm
Si	1 - 10
Mn	2 - 20
Cr	20 - 200
Ni	15 - 150
Mo	3 - 30
Fe	70 - 700

TABLE 5.6: GROSS COMPARISON IN CAPITAL AND OPERATING COSTS [6]

PROCESS	SO_2 Removal Cap. $/kW	SO_2 Removal Op. $/kW-y	SO_2 Removal Energy cons. $J/kgSO_2 \times 10^3$	Disposal Cap. $/kW	Disposal Op. $/kW-y	Products t/kW-y
A. Throw-away, lime	75 - 95	15 - 26	74	30 - 48	8 - 15	0
B. Regenerative						
1. Wellman Lord	94 - 137(a)	17 - 31	109	0	0	0.05 - 0.21 (H_2SO_4)
2. MgO	98 - 137(a)	15 - 25	98	0	0	0.05 - 0.21 (H_2SO_4)
C. Directly saleable (Projected)	75 - 95 (*)	19 - 42 (+)	74(*)	0	0	0.05 - 0.24 ($MgSO_3$)

Notes: Basis - 500 MW; 0.8 - 3.5% S Coal; at 3.5% S; 77,000 t/y SO_2 generated; 95% efficiency; Mid 1979 US $

(a) Regeneration equipment included

(*) Assumed the same as (A)

(+) Difference in lime and MgO assumed to be $220/t

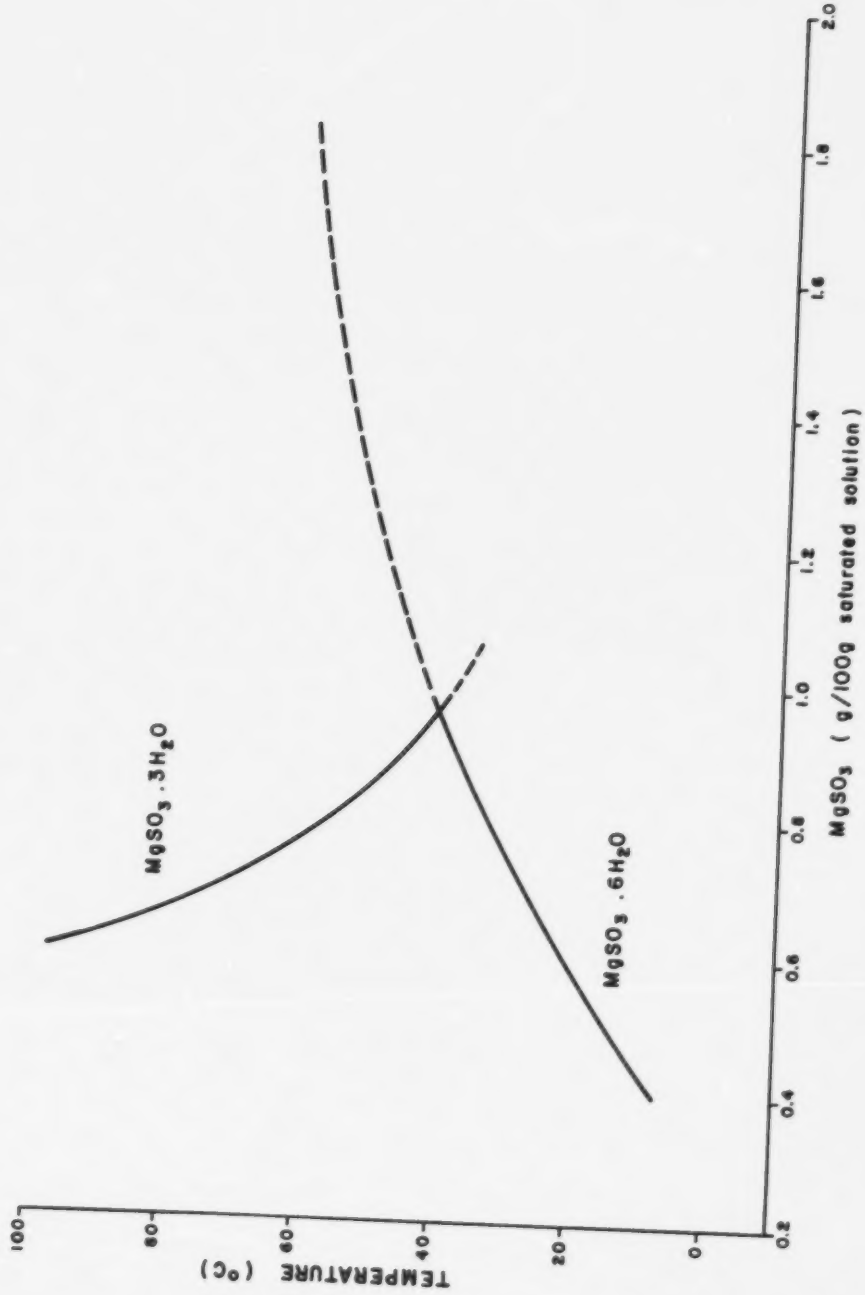


FIGURE 5.6 . $MgSO_3-H_2O$ SYSTEM .(Reference No. 13)

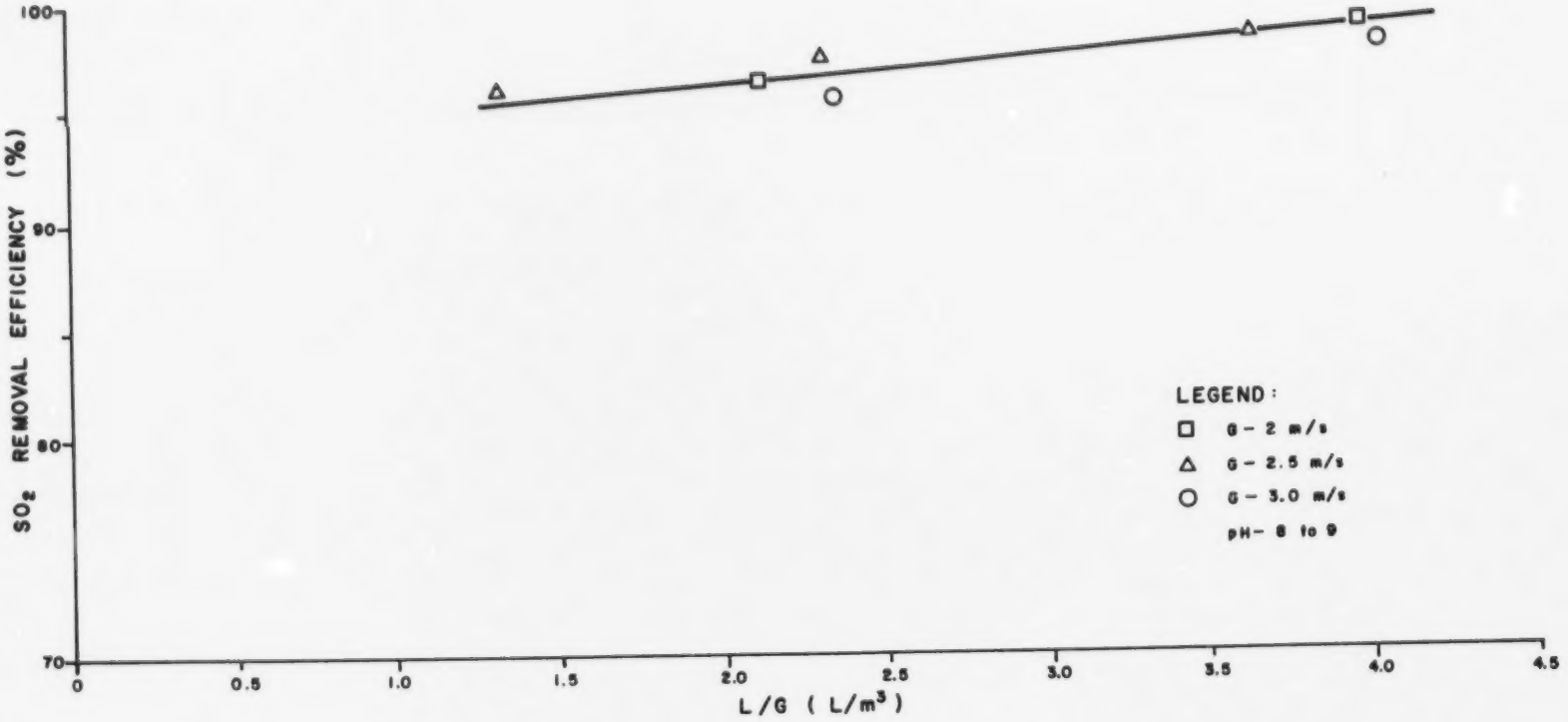


FIGURE 5.1 . VARIATION IN SO_2 REMOVAL EFFICIENCY WITH GAS VELOCITY.

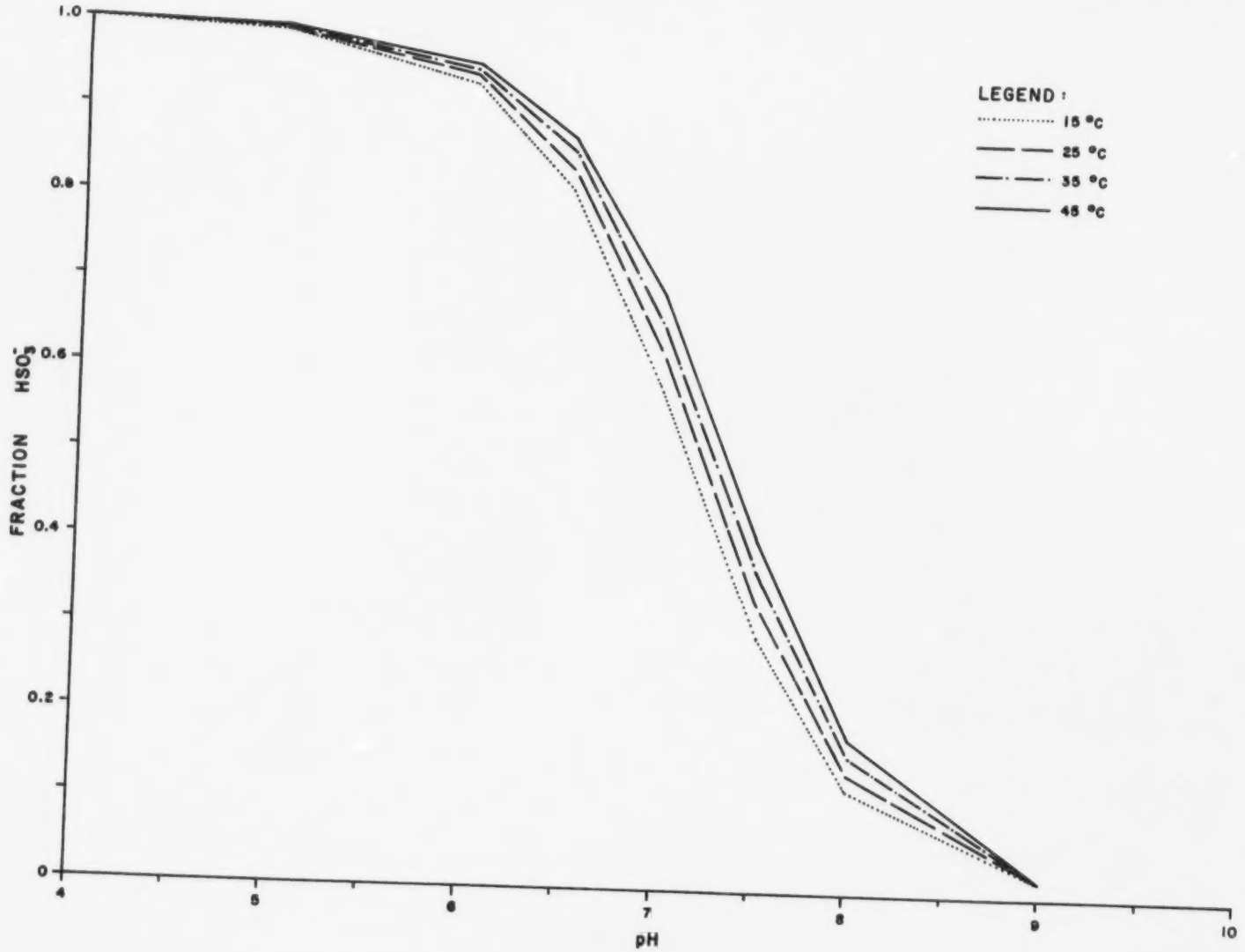
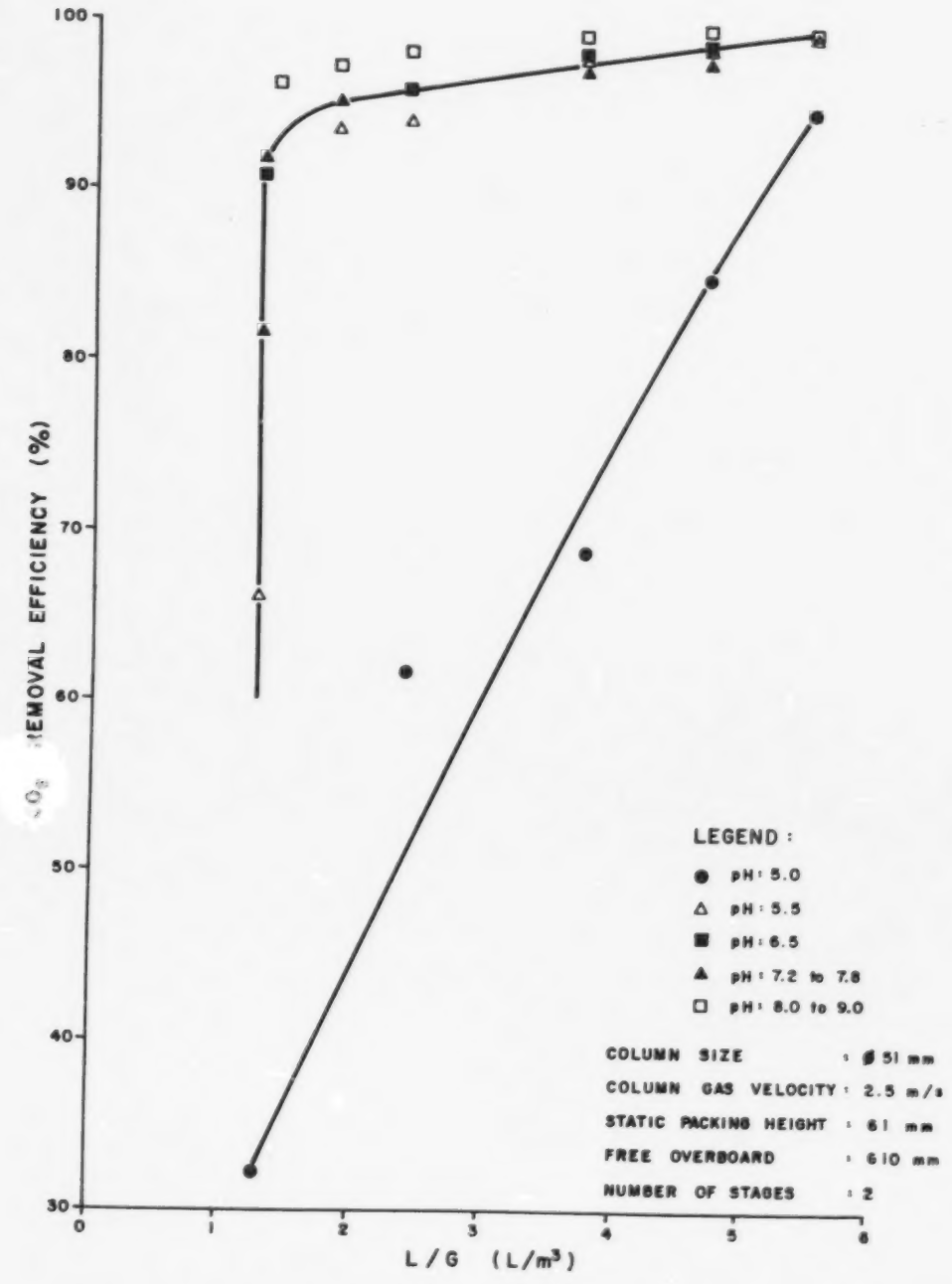


FIGURE 5.2 . HSO_3^- / $SO_3^=$ VARIATION WITH pH .



Inlet SO_2 concentration : 2300 to 10000 ppm

FIGURE 5.3 . VARIATION IN SO_2 REMOVAL EFFICIENCY WITH L/G & SLURRY pH .

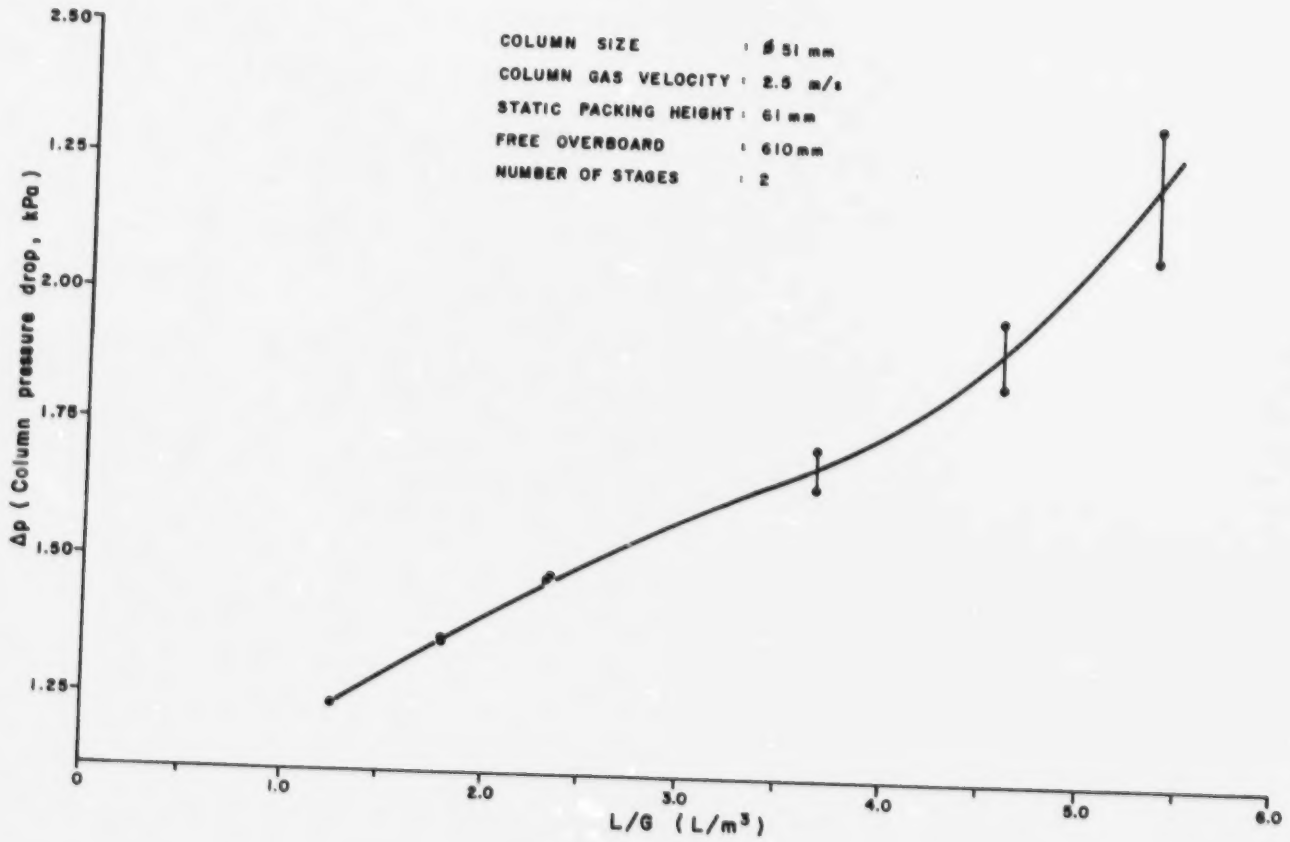


FIGURE 5.4 . VARIATION IN Δp WITH L/G .

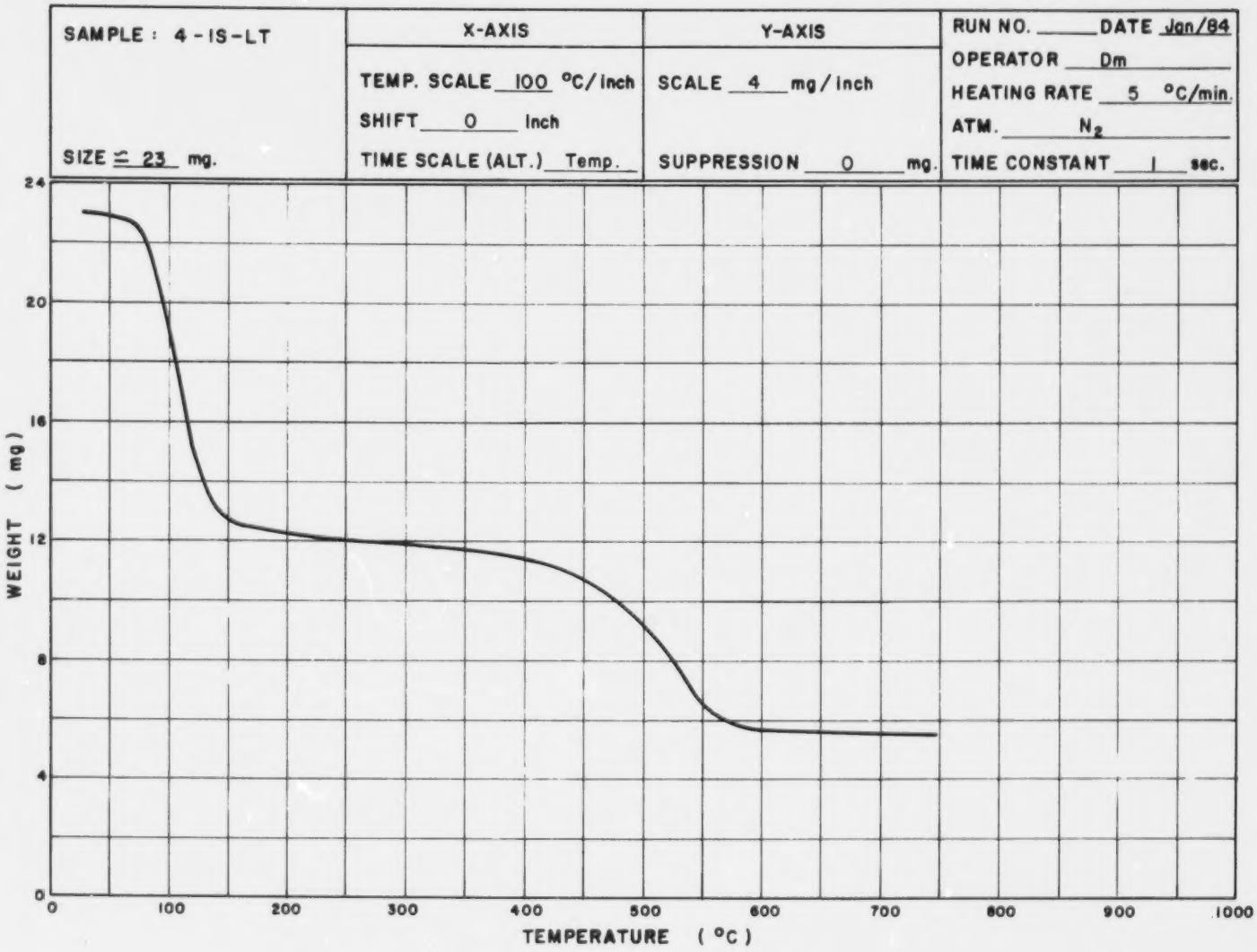


FIGURE 5.5 . EXAMPLE OF TGA RESULTS .

SECTION 6

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APPENDIX A

ABSORPTION REACTION RATE EXPERIMENT

SO_2 absorption in the magnesium-based process could be represented by the following reactions:

$$MgO + SO_2 \rightarrow MgSO_3 \qquad (A.1)$$

$$MgSO_3 + SO_2 + H_2O \rightarrow Mg(HSO_3)_2 \qquad (A.2)$$

As a first step in the scrubbing test, preliminary laboratory tests were conducted to compare qualitatively the above reaction rates. A known weight (4 grams) of dry MgO was added to 100 mL of water in a beaker and SO_2 was bubbled through the liquid at 1 mL/s rate. The pH of the liquid was continuously recorded.

The results are presented in Figure A.1, showing the pH of the liquid as a function of time. In the region AB, SO_2 gas dissolves and hence pH drops quickly. In the region BC, SO_2 reacts with MgO to form $MgSO_3$ (Reaction A.1). When sufficient $MgSO_3$ is formed, the reaction between $MgSO_3$ and SO_2 proceeds (Reaction A.2) causing the pH to drop further (region CD).

The test was repeated using anhydrous $MgSO_3$ instead of MgO and the corresponding results are shown in Figure A.2. It is clear that it is quite similar to the region CD of Figure A.1. From Figure A.1 and A.2 it may be surmised that the SO_2 absorption rate is comparatively much faster by $MgSO_3$ to MgO. Here pH is used as an indicator of the reactions.

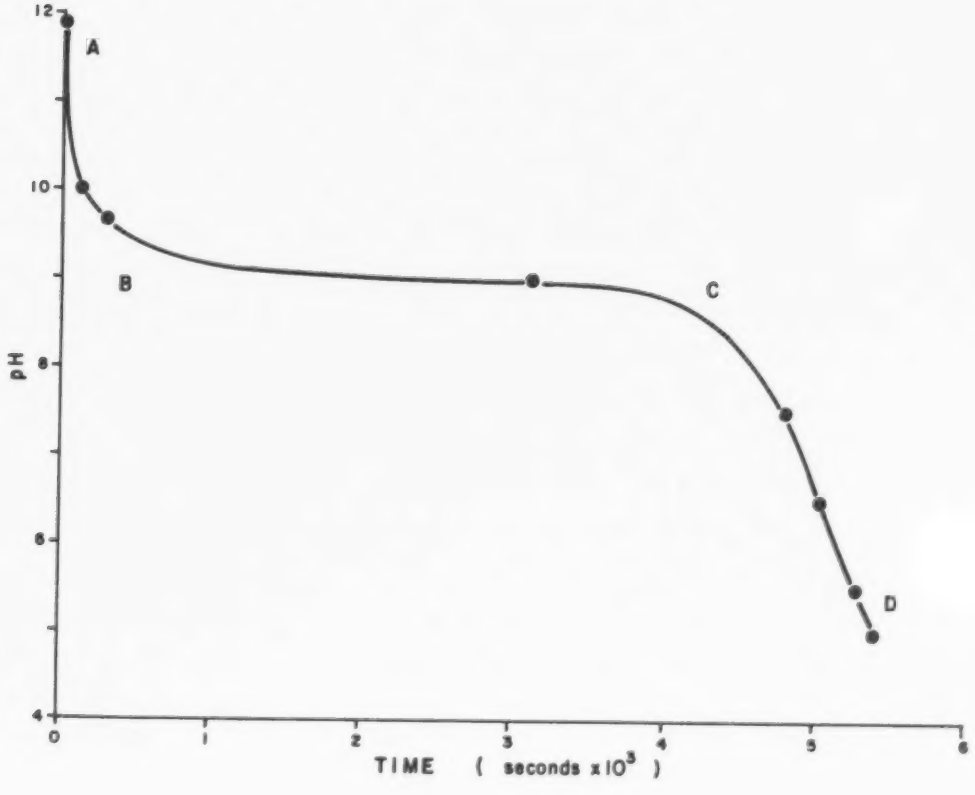

FIGURE A.1 . SO_2 ABSORPTION RATE BY MgO : Variation of pH with time .

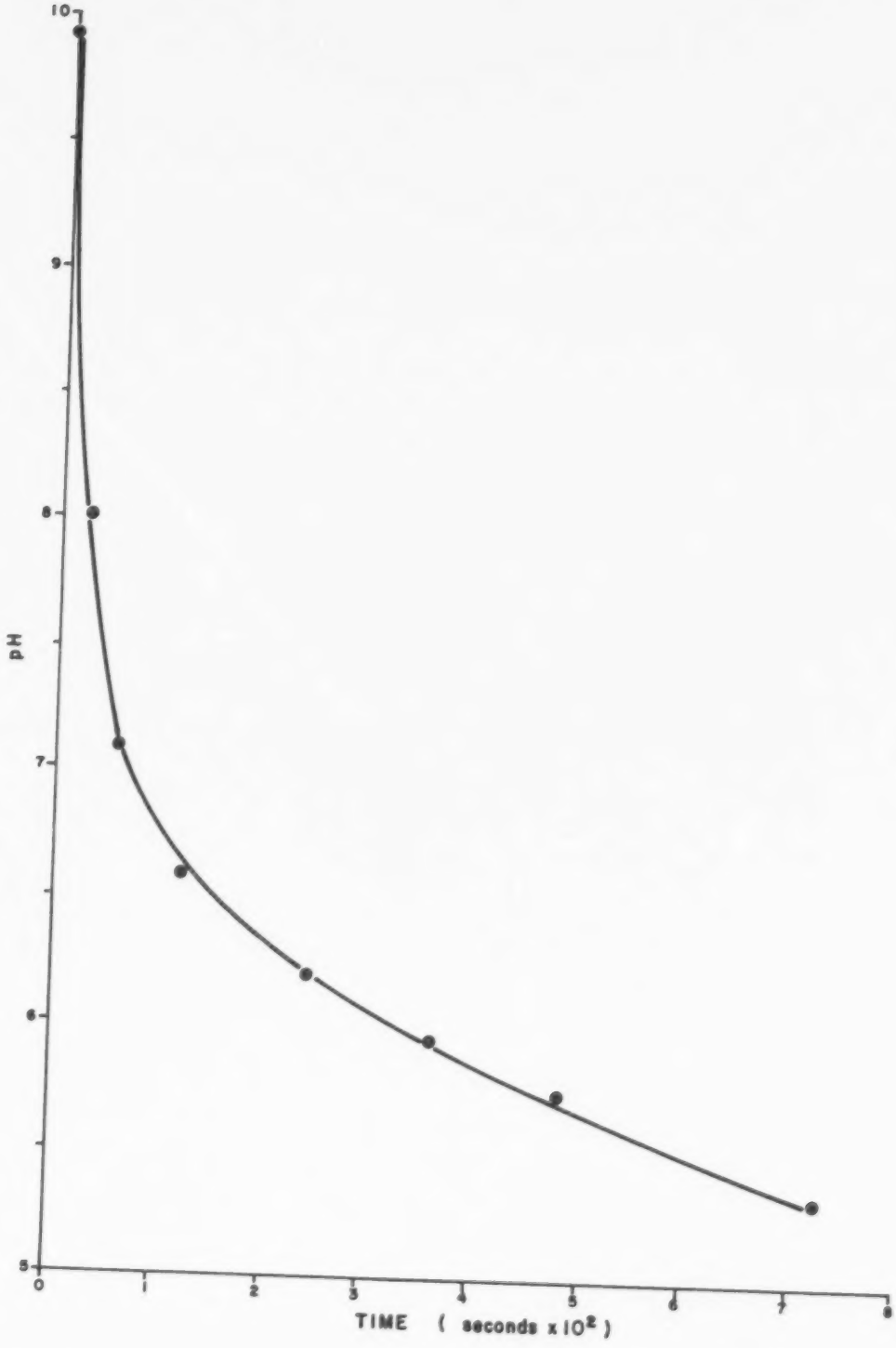

FIGURE A.2 . SO_2 ABSORPTION RATE BY $MgSO_3$: Variation of pH with time .

APPENDIX B

REGENERATION REACTION RATE EXPERIMENT

As mentioned in Section 3, the active absorbing reagent is $MgSO_3$ which reacts with SO_2 to form $Mg(HSO_3)_2$. Thus $MgSO_3$ has to be regenerated, which is carried out in the regeneration tank where slaked MgO, $Mg(OH)_2$, and the scrubber outlet containing mainly $Mg(HSO_3)_2$, are mixed. To obtain an indication of the required residence time for the above regeneration the following tests were carried out.

Laboratory Tests at AEC

To a well mixed $Mg(HSO_3)_2$ solution, at pH value of 5.3, MgO was added in powder form and the pH increase was recorded as a function of time. The pH of the $MgSO_3$ slurry is in the range of 9.5 to 10. Hence the time required to reach pH of approximately 10 is considered as sufficient residence time for the regeneration reaction to "complete". The results of the test are presented in Figure B.1. This shows that, in the presence of excess MgO a residence time of less than 10 minutes is sufficient to regenerate all $Mg(HSO_3)_2$ to $MgSO_3$.

Field Tests

During field tests a sample of the scrubber outlet liquid was collected (pH = 5.6). Batches of 100 mL of the scrubber outlet sample were prepared. Varying amounts of $Mg(OH)_2$ slurry were added (1, 2, 2.25, 2.5 and 3 mL) to the 100 mL samples of the scrubber outlet. The sample was kept well stirred. The variation of the pH with time was used as a measure of the extent of the completion of the reaction. The results are presented in Figure B.2.

A lower pH in the regeneration tank is desirable for preferential SO_2 absorption. Results presented in Section 5 show that a regeneration tank pH in the range 6 to 7.5, is sufficient to achieve high SO_2 absorption efficiency and good purity of the product (low CO_2 absorption). Hence this pH range represents adequate regeneration of $MgSO_3$. Note that (Figure B.2) pH values in the range of 6.2 to 7.5 could be obtained within less than 10 minutes for a wide range of $Mg(OH)_2$ feed.

The above tests indicate that for sizing the regeneration tank a residence time of at least 10 minutes should be provided to allow sufficient regeneration of $MgSO_3$.

FIGURE B.1 . REGENERATION REACTION TEST (lab) : Variation of pH with time .

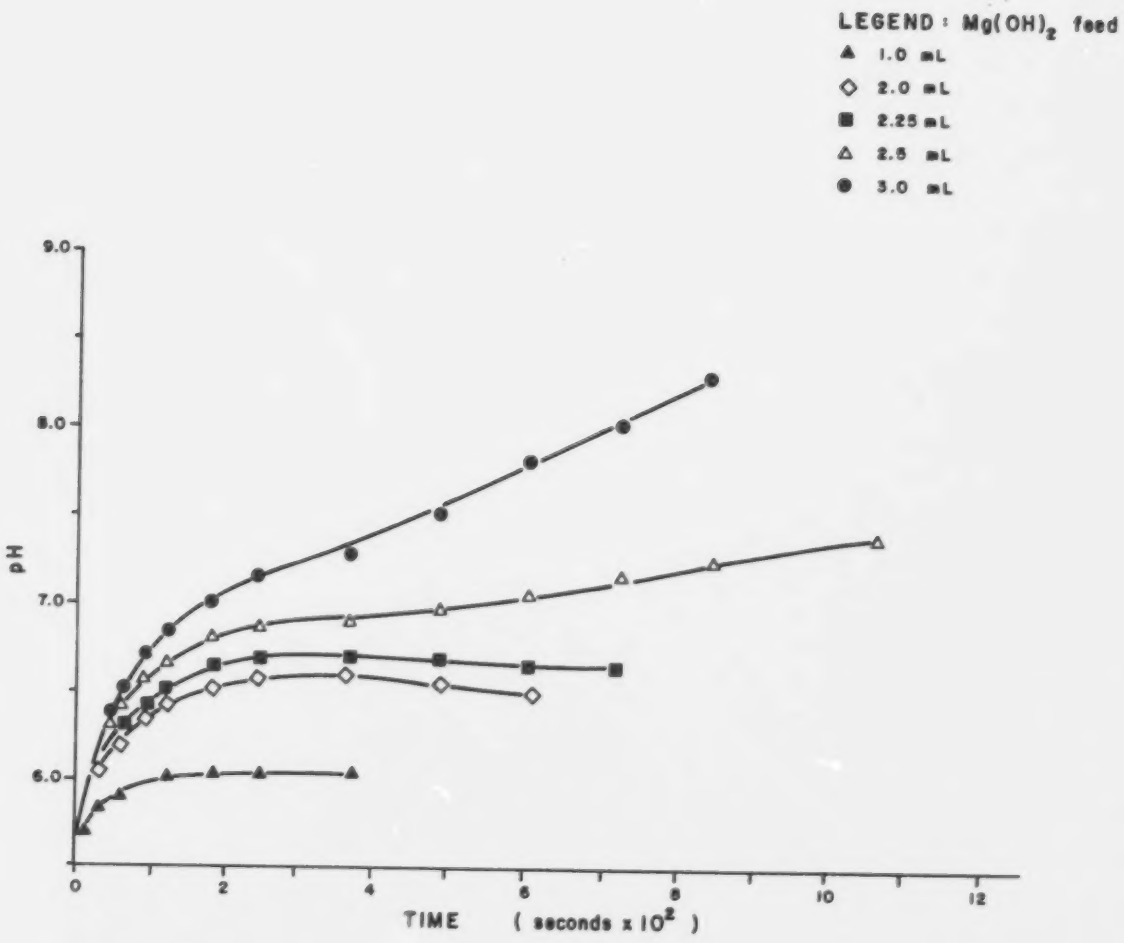

FIGURE B.2 . REGENERATION REACTION TEST (field) : Variation of pH with time .

APPENDIX C

LIQUID HOLD-UP TESTS

The turbulent contactor produces intimate contact between the gas and liquid. Inherently, this type of contactor can handle high gas and liquid flow rates far in excess of those possible in conventional packed towers. The high absorption capacity of the turbulent contactor is due to (1) the packing motion produces turbulence in the liquid phase and (2) the high gas flow rate results in increased liquid hold-up in the absorber. This increases the gas-liquid interfacial area for a given liquid flow rate. The higher the liquid hold-up the longer is the liquid-gas contact time.

To get a qualitative evaluation of the scrubber performance, measurements of liquid hold-up were conducted. For a conventional packed bed absorber the non-dimensional liquid hold-up (h_l) is generally defined as:

$$h_l = \frac{v}{ZA} \qquad (C.1)$$

where v = liquid hold-up volume in the absorber
Z = mean height of packing
A = absorber cross sectioned area

For the turbulent contact absorber the bed height measurement is difficult due to the dynamic nature of the bed. Hence the liquid hold-up volume is used directly instead of expressing it as a dimensionless parameter.

A direct method of liquid hold-up measurement was used in this study. This involved the following steps:

(1) Setting the gas and liquid flow rates to the desired values after the system was stabilized.

(2) Controlling the liquid outlet flow valve at the scrubber outlet to maintain a particular level in the bottom of the absorber section (below the gas entrance and turbulent bed).

(3) Stopping the liquid flow instantaneously to the scrubber and draining the liquid in the column into a graduated cylinder. The test was repeated for various liquid flow rates, keeping the gas flow rate constant (the same used for SO_2 removal efficiency test - Section 5.2). The results are presented in Figure C.1.

Some additional measurements were conducted after reassembling the scrubber unit at AEC. Here the effect of gas flow rate on the liquid hold-up was studied. Ambient cold air was used as the gas and the liquid hold-up was measured as before for a wide range of liquid and gas flow rates. The results are presented in Figure C.2. It may be noted that the amount of liquid hold-up was found to be independent of gas velocity in the absorber but dependent on the liquid flow rate. This is in agreement with previous studies (17).

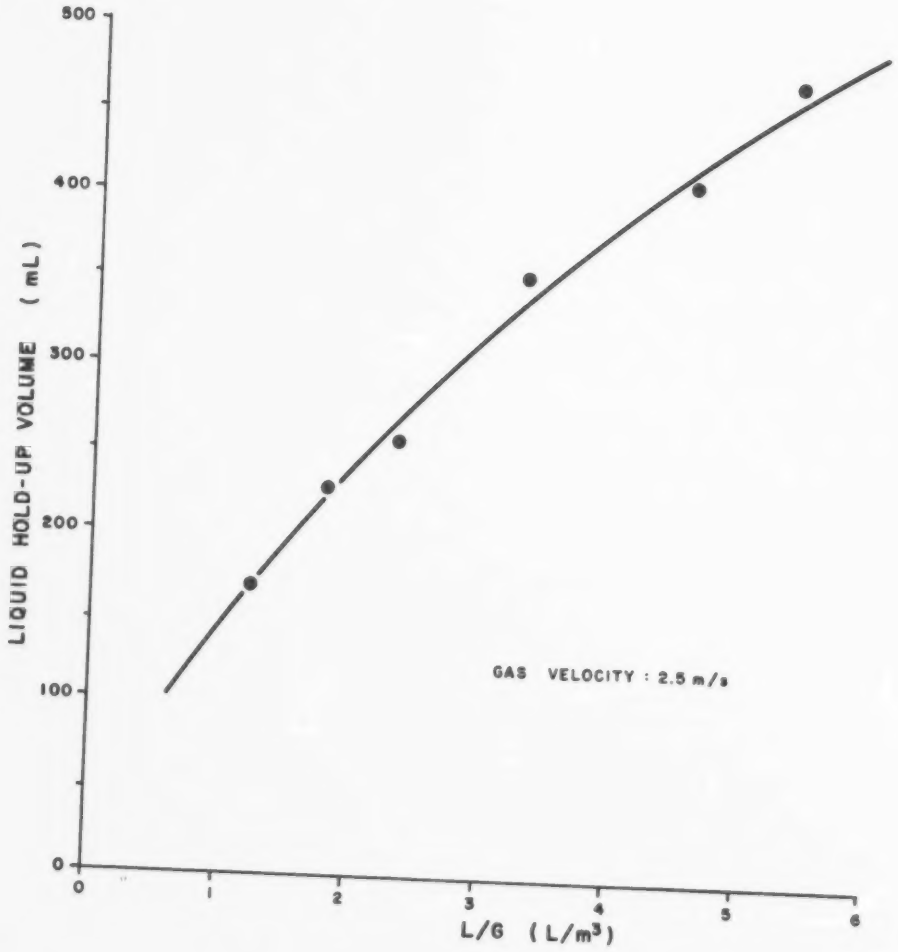

FIGURE C.1 . VARIATION OF LIQUID HOLD-UP WITH L/G .

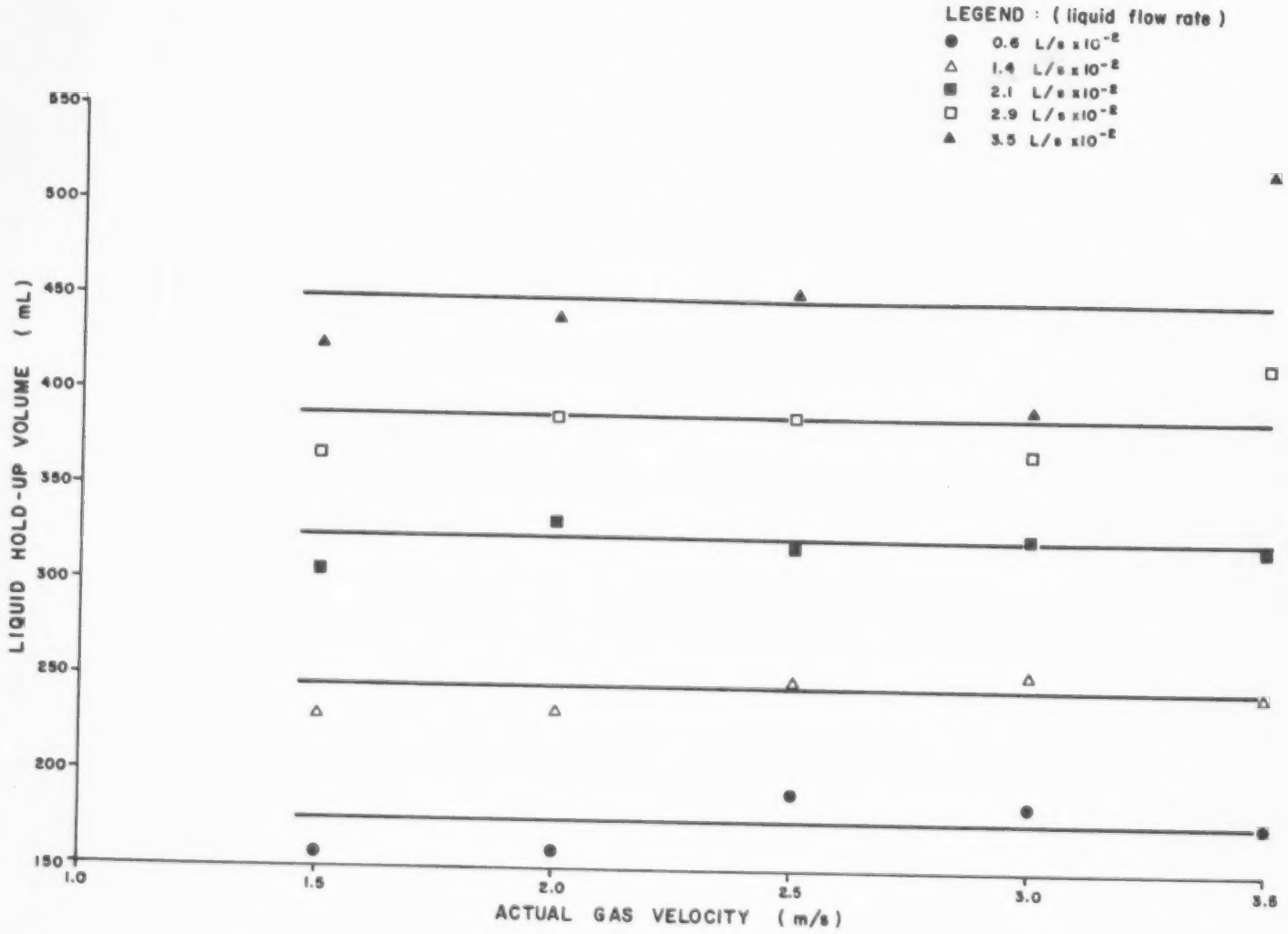

FIGURE C.2 . VARIATION OF LIQUID HOLD-UP WITH GAS VELOCITY AND LIQUID FLOW RATE .

APPENDIX D

ANALYTICAL METHODS

Sulphur and metals were measured using ISA Model JY38P sequential, inductively coupled plasma spectrometer. The system employed a one meter monochrometer, a 3600 line grating and a 27.12 MHz radio frequency generator. Metals were measured using a forward power of 1 kW, whereas sulphur was determined using 1.5 kW. Standards were prepared from "five nines" purity standards (SPEX) and 15 megohm (or better) water.

Sulphur Analysis

Liquid samples (25 mL) were combined with hydrogen peroxide (25 mL, 30%, Aristar) and made up to 100 mL with water.

Solid samples were first dried overnight at 60°C and approximately 50mg was weighed into a volumetric flask. To the flask were added 10 mL of water, 15 mL of hydrogen peroxide (30%, Aristar). To this 2 mL of nitric acid (Aristar) were added dropwise, slowly with swirling. With this procedure sulphite and sulphur dioxide were oxidised to sulphate without loss. The volume was then made up to 50 mL.

Further dilution was generally unnecessary. The samples were aspirated into the flame without additional treatment.

Metal Analysis

Liquid samples did not require any pretreatment and were aspirated directly into the spectrometer. Samples of particularly high concentration were diluted prior to analysis. Generally the sample used for sulphur analysis was used for metals analysis.

The solid samples prepared for analysis of sulphur as described above were also used for metal analysis.

ICP Spectrometer Calibration

Various emission lines were used for the analysis depending on the concentration of the standards and samples. For sulphur the line at 181.974 nm was employed with standard concentrations of 100 to 1000ppm. For calcium, iron and manganese the lines at 317.933, 275.574 and 260.569 nm respectively were used, with concentrations of 0.5 to 50 ppm. Determinations of magnesium were made at various positions: 277.983 nm (weak line), 279.079 nm (medium line) and 279.806 nm (strong line) using concentrations varying between 10 and 1000 ppm.

Calibrations were determined in triplicate, and calibration curves were a first order fit.

The instrument employed carbon lines for initialization: 193.026 nm for sulphur determinations and 147.856 nm for metal determinations.

High and low standards were run with samples to check the consistency of calibration. When necessary a recalibration routine was run.

Carbon Analysis

A Beckman Tocamaster 915B carbon analyser equipped with two channels (total carbon and inorganic carbon) was used to determine carbon. The inorganic channel was employed in this series of determinations. It contains quartz chips impregnated with phosphoric acid and maintained at 150 degrees celsius. When an aqueous solution containing carbonate/bicarbonate is injected carbon dioxide is evolved and detected by a non-dispersive infra-red detector. The equipment is calibrated with sodium carbonate standards (e.g. 0, 50 and 100 ppm carbon) allowing the carbonate in the sample to be calculated.

Liquid samples were injected directly or diluted (1+9 water) to bring into range (50 microlitres, 50ppm full scale response).

Solid samples were rather more difficult to measure because of the low carbonate to sulphite ratio and the very low solubility of magnesium carbonate. A suspension of magnesium salts from the scrubber (or standards) containing

approximately 500 mg of solid was placed in a 500 mL wash bottle. This was stirred and a slow stream of nitrogen (carbon dioxide free) passed through the suspension. Concentrated hydrochloric acid was slowly introduced until the pH was 4. The pH was readily monitored by the use of a universal indicator. As the acid was introduced carbon dioxide was evolved and swept out by the nitrogen stream. It was passed into a second wash bottle containing dilute sodium hydroxide solution and trapped as sodium carbonate. Universal indicator was again used to make sure there was always excess base.

The solution was then injected into the Tocamaster as for liquid samples. Knowing the initial weight of magnesium salts allows the percent carbonate to be calculated.

By maintaining the pH at 4 or more it was observed that sulphur dioxide was not evolved with the carbon dioxide.

APPENDIX E

UNCERTAINTIES IN CAPITAL AND OPERATING COSTS OF A SCRUBBER

In selecting a scrubber for a particular application, various factors must be considered. These include the selection of an appropriate process - for example, in terms of system performance and reliability, and potential operating problems - and capital and operating costs.

Information from the literature and from existing installations are available and could provide a guide. However, it could rarely be directly used for decision making. Local, site-specific conditions are often the dominant factor, thereby making it very difficult to transfer information from one application to another.

A summary of a survey is presented to show the wide variation in capital cost of a scrubber, and hence the difficulties in transferring such information for estimating the capital cost of a site-specific installation. Figure V.1 shows the variation in capital cost with scrubber capacity and scrubbing process. Note therefore that:

(1) Even for the same process, for example the lime process, the capital costs were in the range from $29/kW for a 85 MW unit to $175/kW for a 825 MW unit; and for the sodium carbonate process, from $48/kW to $127/kW for the same capacity unit. Terms such as average or mean cost would thus have little significance. Note, furthermore, the anomalous trend of increasing cost per unit capacity with increasing capacity.

(2) Comparison between the Wellman-Lord and the lime process shows that the former could have a lower cost: $133/kW vs. $175/kW. This is contrary to what is expected in that the Wellman-Lord process, being regenerative is inherently more capital intensive.

The wide variation in capital cost is also found in "paper estimates". It was quoted[6] that a scrubber supplier claimed that it could install a limestone scrubber at a cost of $75/kW, whereas the user's estimate - for the same system and scope - was $145/kW.

Such a wide variation also exists in operating cost. In that same survey, the annual operating costs were in the range from 1.02 to 18.66 mills/kWh for the lime process. There was no apparent trend that could be related to scrubber capacity, efficiency or sulphur content in the coal.

There could be numerous reasons for the wide variations in capital and operating costs. Regardless of what these might be, it is apparent that it would be unsound to estimate the cost of a scrubber for a site-specific application based solely on "paper estimates" and literature information.

It is our contention, therefore, that on-site pilot plant testing is necessary for obtaining relevant and realistic assessment of a process, not only in terms of capital and operating cost, but also in terms of process suitability.

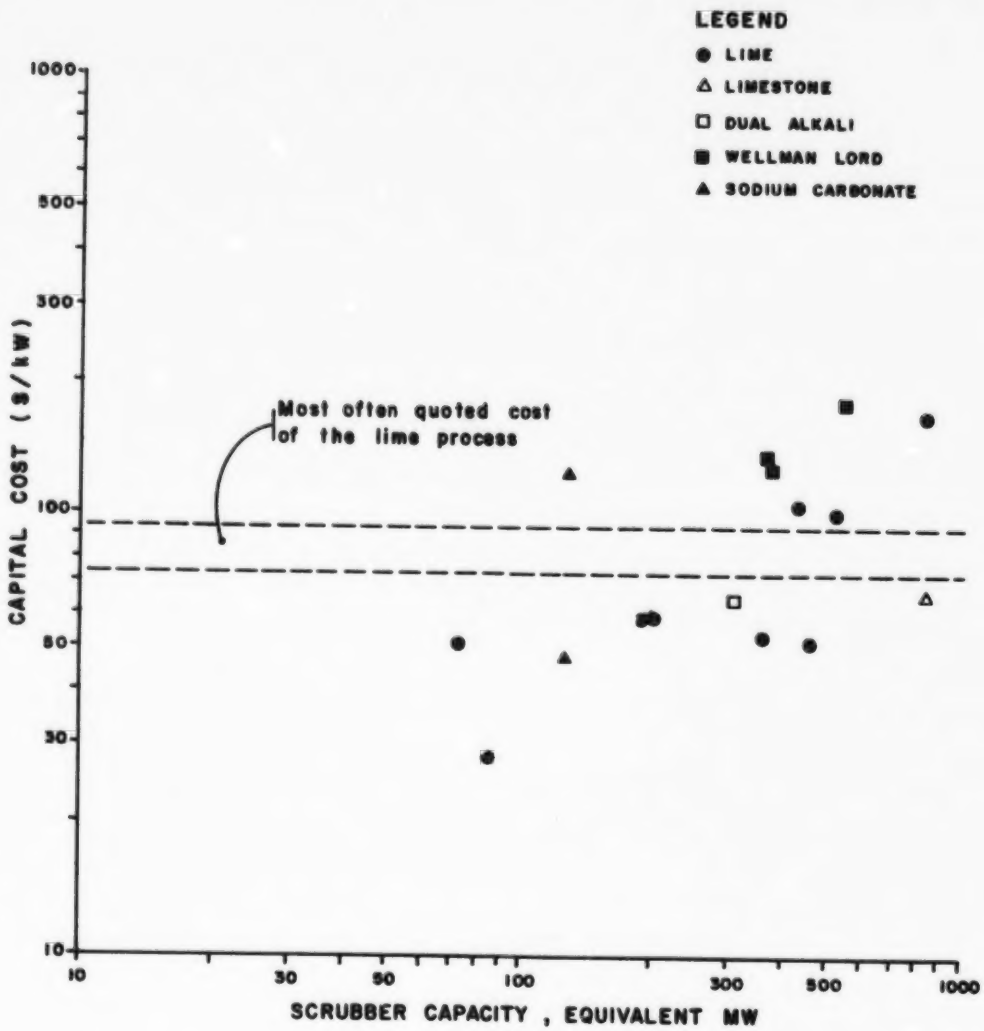

FIGURE E.1 . VARIATION IN CAPITAL COST WITH SCRUBBER CAPACITY AND SCRUBBING PROCESS .